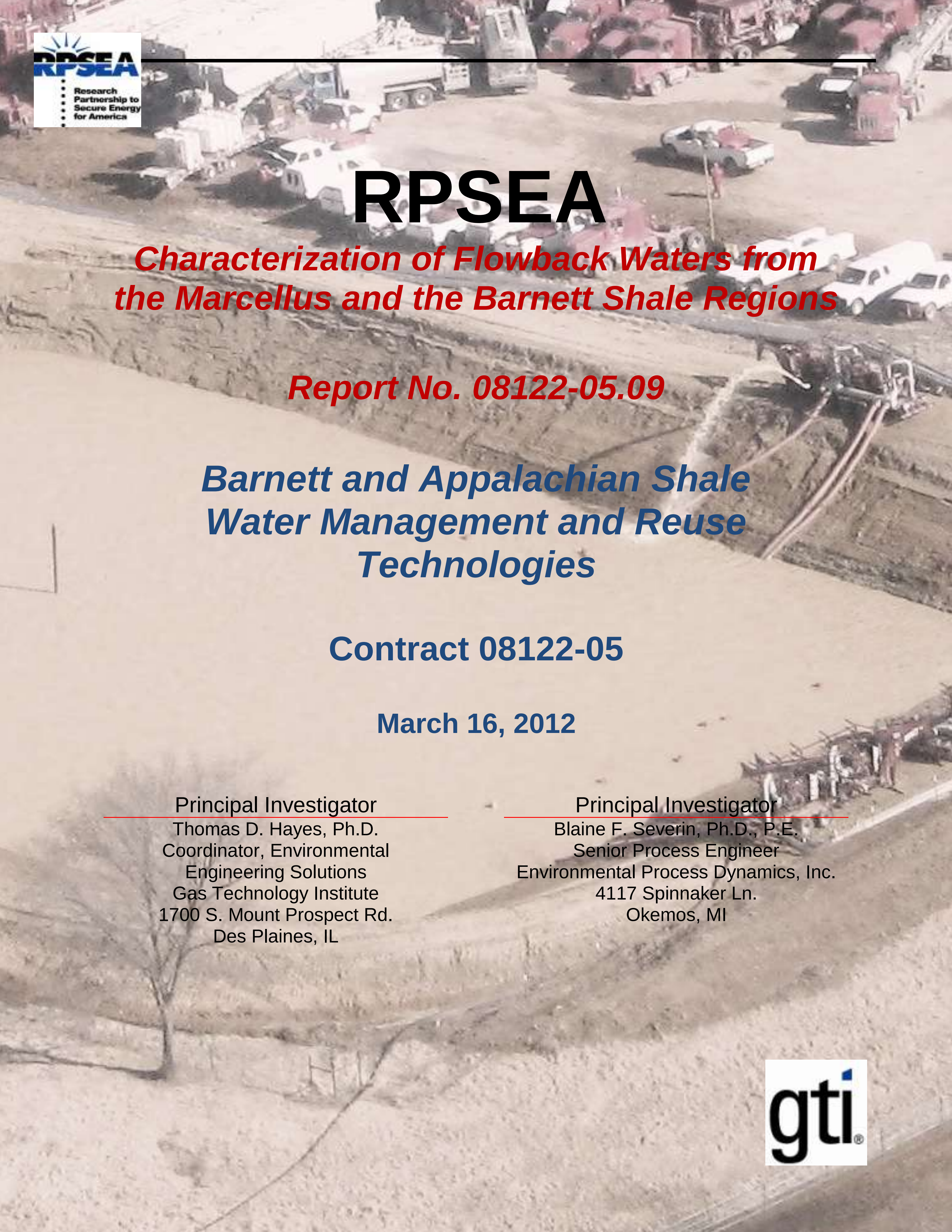

RPSEA

Characterization of Flowback Waters from the Marcellus and the Barnett Shale Regions

Report No. 08122-05.09

Barnett and Appalachian Shale Water Management and Reuse Technologies

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Principal Investigator
Thomas D. Hayes, Ph.D.
Coordinator, Environmental Engineering Solutions
Gas Technology Institute
1700 S. Mount Prospect Rd.
Des Plaines, IL

Principal Investigator
Blaine F. Severin, Ph.D., P.E.
Senior Process Engineer
Environmental Process Dynamics, Inc.
4117 Spinnaker Ln.
Okemos, MI

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Acronym	Definition		Acronym	Definition
ASWCMC	Appalachian Shale Water Conservation and Management Coalition		PPM	Part per million (≈mg/l)
BBL/bbl	Barrel (42 gallons)		PA-DEP	Pennsylvania Department of Environmental Protection
BCF	Billion Cubic Feet		PPB	Part per billion (≈µg/l)
BTEX	Benzene, Toluene, Ethylbenzene, Xylenes		POGAM	Pennsylvania Oil & Gas Association
Flowback Water	The water stream that flows from a well in the weeks following hydraulic fracturing completion		QAPP	Quality Assurance Project Plan
Frack	Hydraulic Fracture		TCF	Trillion Cubic Feet
Frac Job	Well completion event involving hydraulic fracturing		TDS	Total Dissolved Solids
FSAP	Field Sampling and Analysis Plan		TPH	Total Petroleum Hydrocarbons
mg/l	Milligrams per liter		PCB	Polychlorinated Biphenyl Compound
µg/l	Micrograms per liter		POTW	Publicly Owned Treatment Works (a Sewage Treatment Facility)
MSC	Marcellus Shale Coalition		WV-DEP	West Virginia Department of Environmental Protection

EXECUTIVE SUMMARY

The hydraulic fracturing of shale for the development of unconventional natural gas sources has such great potential that it is often touted as an energy revolution. With all the positive economic upside to the development of this resource, detractors to the industry question the potential environmental impact of the process. Good water management is essential to the economic sustainability of the industry. Unfortunately, the public literature is replete with anecdotal evidence. There remains a dearth of sound scientific publications on which rational decisions may be made. The purpose of this report is help address water management issues by elucidating the chemical nature of flowback waters. Hopefully, this knowledge may be used to help develop sustainable water management plans.

This report covers recent sampling of flowback water from 19 sites in the Marcellus region of Pennsylvania and West Virginia and 5 sites from the Barnett region of northern Texas. The database includes flowback rates, volumes, and chemical analyses of the injected water and the recovered flowback water. Chemical analyses include general chemical information typically used for drinking water analyses. Additionally, the waters were tested for 70 volatile organics, 116 semi-volatile organics, 22 pesticides, PCB's, and 27 metals. The list of chemicals evaluated for this project was co-developed by industrial partners, and state environmental agency representatives.

The data are of interest for a couple of discernable trends, such as increased salts (total dissolved solids) and decreased flow with time. The main salt composition appears to be sodium chloride. Chloride accounts for more than 93% of the available anionic content. Some sulfate (500-1000 ppm range) is present in the Barnett samples, but is very low in the Marcellus samples (<100 ppm). Carbonate alkalinity, the main pH buffering system in natural waters is quite low (<150 ppm). The commonly observed cations are sodium, calcium, barium, strontium, and iron. The low alkalinity and sulfate concentrations are keys to understanding the relative abundance of the various cation species. They are also keys to understanding the range and capability of treatment/reuse options for the prevention of scale build-up. Heavy metals (other than iron) are generally either not detected, or in very trace concentrations, and generally far less concentrated than levels present in municipal wastewater sludge.

Other components, such as the aromatics such as benzene, toluene, ethyl benzene, and toluene (BTEX) and other organic compounds, such as naphthalene, that are commonly associated with petroleum sites tend to be present only in low to trace concentrations (ug/l to ppm) without a discernable pattern with time. Heavier polynuclear aromatic hydrocarbon compounds (PAH's) --- such as commonly seen in petroleum wastewater --- are generally not present in the flowback water, and occur occasionally in only very trace concentrations. These compounds are considered by the wastewater treatment industry to be highly treatable. Several standard treatment methods are available to handle these types of compounds at these low levels.

Compounds that can originate from human sources, such as pyridine and the general class of phthalate esters, are found in less than 50% of the samples. Methylated phenols are more commonly encountered, but only in concentrations between 10 to 100 ppb. Halogenated compounds are rarely encountered. One pesticide was detected (<0.05 ppb) in one sample (out of 79) and was likely an error. PCB's were not detected in any samples.

Most of the organic chemical analyses performed resulted in "non-detects." These non-observations are vital to begin the discussion of what "not to look for" when performing analyses on shale gas waters. It is important to focus engineering and planning resources on the chemistry that is present, and to avoid effort in fruitless areas.

INTRODUCTION

The Marcellus shale formation is the largest known shale deposit in the world. It overlies much of the Appalachian Basin from West Virginia in the south, to Upstate New York in the north, and Ohio to the west. The recoverable reserves of natural gas in the Marcellus shale have been estimated at more than 489 trillion cubic feet (Engelder, 2008). Recent advances in horizontal drilling and multi-stage hydraulic fracturing technologies have made sustainable natural gas production viable from otherwise uneconomical, unconventional shale reservoirs such as the Barnett, Haynesville, Fayetteville, Woodford, et al. These tools and technologies have been successfully applied and currently enable the ongoing and the future development of these shales.

Many of the logistical challenges associated with the development of shale gas stem from the large amounts of water associated with the completion and operation of shale gas wells that must be transported, stored and disposed of in a manner that is protective of human health and the environment. In the course of developing shale gas in the Barnett and the Marcellus Shale, thousands of wells will be drilled and completed. Hydraulic fracturing (“fracking”) is a necessary step for the completion of each of these wells in order to achieve economic well performance in terms of natural gas production. This step requires between 1 and 4 million gallons (23,800 and 95,200 bbl) of water for successful completion of each well; vertical wells require approximately 1 million gallons (23,800 bbl) and horizontal wells require 3-4 million gallons (71,400 to 95,200 bbl) (Gaudlip, et al., 2008).

During a typical “fracK job,” water is pumped downhole while chemicals such as friction reducers and various grades of sand are introduced to ensure a successful fracture of the shale. Following hydraulic fracturing, a fraction of the water (approximately 25%) that was injected is collected over several days resulting in the collection of a “flowback” water stream that contains salts, oils and greases, and soluble organics (volatile and semi volatile) that accumulated in the water downhole. Flowback water also contains low concentrations of chemicals that are introduced during the frack job which normally include friction reducing polymers, corrosion inhibitors, scale inhibitors, and biocides. These additives facilitate the hydraulic fracturing process and prevent problems with well operation.

The first steps in identifying effective water management alternatives include an effective analysis of the characteristics of the water streams involved in shale gas development. The overall objective of this project is to develop an information base on the nature and composition of influent water and flowback waters associated with completions of shale gas wells in the Marcellus and Barnett Shales.

METHODS AND PROCEDURES

Upon request to the Marcellus Shale Coalition (MSC), 17 member companies of the MSC volunteered 19 locations for the sampling of influent and effluent water streams. Two companies provided access to five sites in the Barnett. At each location, a well completion was conducted using hydraulic fracturing procedures that involved the injection of an influent stream of water and the subsequent collection of flowback water. Standard procedures were used to conduct sampling and analysis needed for the development of water characterization data. All sampling was performed by the GTI subcontractor, URS, following the same standard procedures. All sample analyses were performed by a single laboratory, Test America of Pittsburgh, PA. Test America, an independent analytical laboratory, provided the appropriate sample containers, preservatives and completed the analytical analyses. Test America is certified in West Virginia and Pennsylvania. Data tabulation, analysis and information base development was provided by the Gas Technology Institute for this effort.

Details of the methods and procedures used for the collection and analysis of samples obtained from each of the 19 locations are found in the Field Sampling and Analysis Plan (FSAP) which is located in Appendix A. The Field Sampling and Analysis Plan (FSAP) was developed to ensure that the data and information gathered for the flowback characterization study was properly collected and documented.

A major aim of the characterization study was to generate technically sound data. To meet this objective a Quality Assurance Project Plan (QAPP) was used to generate accurate, precise, representative and complete data; this document is provided in Appendix B. The QAPP provided the specific quality assurance/quality control (QA/QC) procedures executed during the flowback Characterization Study.

Together, the FSAP and QAPP comprise the Sampling and Analysis Plan (SAP). The SAP was designed to meet the following informational goals:

- Identify specific constituents of interest (COI) associated with flowback water;
- Determine whether hydraulic fracturing additives are a source of COI in the management of water associated with shale gas development; and,
- Provide sufficient information for the selection of proper water management and disposal techniques.

Prior to initiating the characterization study, the SAP was reviewed by regulatory officials from the Pennsylvania Department of Environmental Protection (PADEP) and the West Virginia Department of Environmental Protection (WVDEP).

The original SAP proposed that four (4) grab samples from six (6) vertical or horizontal well locations be collected throughout West Virginia and Pennsylvania. The following grab samples were proposed:

- One baseline fracturing water sample that includes the fracturing chemicals, excluding the sand;
- Flowback water samples will be collected on days 1, 5 and 14 of the following the fracturing process; and
- Water from an existing producing well at 90 days following hydraulic fracturing.

A similar plan was developed for sites in the Barnett with projected collection on days 1, 3, 5, and 10.

The list of constituents recommended for the characterization study was developed from comments received from the PADEP, the WVDEP and members of the Appalachian Shale Water Conservation and Management Committee (ASWCMC). Because the recommended list of constituents was extremely extensive, it was decided that one sample from each site would be completed for the full list of recommended constituents. All other samples were collected and analyzed for a subset of these constituents, which was designed based on generator knowledge.

The constituents analyzed also include the 56 parameters currently included on the PA-DEP Form 26R instructions. This list of parameters is currently undergoing review and changes are being considered given that much has learned since that list was initially included on the instruction form. Also, it may be appropriate to address concerns on a media and program specific basis in lieu of the approach suggested by the Form 26R instructions.

To be consistent with this form, the ASWCMC and MSC modified the sampling program to include additional constituents. More locations were also included to assist operators meet disposal requirements in newly developed areas.

Following the first few rounds of sampling, industry identified a data gap with respect to characterizing the supply water used for fracturing. Supply water is identified as the water used for fracturing prior to introducing the fracking additives.

The updated protocol characterization study called for the collection of five (5) grab samples from the each of the locations and expanded the sampling effort to encompass 19 well locations volunteered by 17 member companies of the Marcellus Shale Coalition. The plan for the Barnett samples called for collection of four (4) samples at five sites. Table 1 presents the list of all of the constituents of interest (by category) that formed the basis for sample analysis. Analytical methods used to perform the various determinations are listed in Table 2.

Table 1. Measurements and Determinations.

General Chemistry		
pH Acidity Total Alkalinity Hardness as CaCO3 Total Suspended Solids Turbidity Chloride Total Dissolved Solids Specific Conductance	Total Kjeldahl Nitrogen Ammonia Nitrogen Nitrate-Nitrite Nitrite as N Biochemical Oxygen Demand Chemical Oxygen Demand Total Organic Carbon (TOC) Dissolved Organic Carbon	Oil & Grease (HEM) Cyanide, Total Amenable Cyanide Bromide Fluoride Total Sulfide Sulfate Total Phosphorus Total Recoverable Phenolics
Volatile Compounds		
1, 4 - Dichlorobenzene 1, 3 - Dichloropropane 2, 2 - Dichloropropane 1, 1 - Dichloropropene p - Isopropyltoluene Naphthalene n - Propylbenzene 1, 2, 3 - Trichlorobenzene 1, 2, 4 - Trichlorobenzene 1, 2, 4 - Trimethylbenzene 1, 3, 5 - Trimethylbenzene Benzyl chloride Isopropylbenzene 2 – Butanone Methyl tert - butyl ether (MTBE) Xylenes (total) 2 - Chloroethyl vinyl ether cis - 1, 2 - Dichloroethene Bromobenzene n - Butylbenzene sec - Butylbenzene tert - Butylbenzene 4 - Chlorotoluene 1, 2 - Dichlorobenzene	1, 3 – Dichlorobenzene Acetone Acrolein Acrylonitrile Benzene Bromodichloromethane Bromoform Bromomethane Carbon disulfide Carbon tetrachloride Chlorobenzene Chloroethane Chloroform Chloromethane Dibromochloromethane 1, 2 - Dibromo - 3 – chloropropane 1, 2 - Dibromoethane (EDB) Dibromomethane Dichlorodifluoromethane 1, 1 – Dichloroethane 1, 2 – Dichloroethane 1, 1 – Dichloroethene trans - 1, 2 - Dichloroethene 1, 2 - Dichloropropane	cis - 1, 3 - Dichloropropene trans-1, 3 - Dichloropropene 1, 4 – Dioxane Ethylbenzene Ethylene Glycol 2 - Hexanone Methylene chloride 4 - Methyl - 2 - pentanone (MIBK) Styrene 1, 1, 1, 2 - Tetrachloroethane 1, 1, 2, 2 - Tetrachloroethane Tetrachloroethene Toluene 1, 1, 1 - Trichloroethane 1, 1, 2 - Trichloroethane Trichloroethene Trichlorofluoromethane 1, 2, 3 - Trichloropropane Vinyl acetate Vinyl chloride Tert - butyl acetate tetrahydrofuran 1 - chloro - 4 - trifluoromethylbenz
Semi volatile Compounds		
Diphenylamine Benzidine bis (2 - Chloroisopropyl) ether 1, 4 – Dioxane 1, 2 – Diphenylhydrazine Acenaphthene Acenaphthylene Acetophenone 2 – Acetylaminofluorene 4 – Aminobiphenyl Aniline Benzo (a) anthracene Benzo (a) pyrene Benzo (b) fluoranthene Benzo (ghi) perylene Benzo (k) fluoranthene Benzyl alcohol	Diethyl phthalate Dimethoate p - Dimethylaminoazobenzene 7, 12 - Dimethylbenz (a) – anthracene 2, 4 – Dimethylphenol Dimethyl phthalate Di - n - octyl phthalate 1, 3 – Dinitrobenzene 4, 6 - Dinitro - 2 – methylphenol 2, 4 – Dinitrophenol 2, 4 – Dinitrotoluene 2, 6 – Dinitrotoluene Dinoseb Disulfoton Ethyl methanesulfonate Fluoranthene Fluorene	Nitrobenzene 2 - Nitrophenol 4 - Nitrophenol N - Nitrosodi - n - butylamine N - Nitrosodiethylamine N - Nitrosodimethylamine N - Nitrosodi - n - propylamine N - Nitrosodiphenylamine N – Nitrosomethylethylamine N – Nitrosomorpholine N – Nitrosopiperidine N – Nitrosopyrrolidine 5 - Nitro - o – Toluidine Parathion Pentachlorobenzene Pentachloroethane Pentachloronitrobenzene

bis (2 - Chloroethoxy) methane bis (2 - Chloroethyl) – ether bis (2 - Ethylhexyl) phthalate 4 - Bromophenyl phenyl ether Butyl benzyl phthalate 4 – Chloroaniline 4 - Chloro - 3 – methylphenol 2 – Chloronaphthalene 2 – Chlorophenol 4 - Chlorophenyl phenyl ether Chrysene Diallate Dibenz (a, h) anthracene Dibenzofuran Di - n butyl phthalate 1, 2 – Dichlorobenzene 1, 3 – Dichlorobenzene 1, 4 – Dichlorobenzene 3, 3' – Dichlorobenzidine 2, 4 – Dichlorophenol 2, 6 – Dichlorophenol	Hexachlorobenzene Hexachlorobutadiene Hexachlorocyclopentadiene Hexachloroethane Hexachloropropene Indeno (1, 2, 3 - cd) pyrene Isodrin Isophorone Isosafrole 3 - Methylcholanthrene Methyl methanesulfonate 2 - Methylnaphthalene 2 – Methylphenol 3 - Methylphenol & 4 – Methylphenol Naphthalene 1, 4 - Naphthoquinone 1 – Naphthylamine 2 – Naphthylamine 2 – Nitroaniline 3 – Nitroaniline 4 – Nitroaniline	Pentachlorophenol Phenanthrene Phenol Phorate 2 – Picoline Pronamide Pyrene Pyridine Safrole 1, 2, 4, 5 – Tetrachlorobenzene 2, 3, 4, 6 Tetrachlorophenol Thionazin o – Toluidine 1, 2, 4 – Trichlorobenzene 2, 4, 5 – Trichlorophenol 2, 4, 6 – Trichlorophenol O, O, O – Triethylphosphorothioate Chlorobenzilate Aramite
Metals		
Aluminum Antimony Arsenic Barium Beryllium Boron Calcium Cadmium Cobalt	Chromium Trivalent Chromium Copper Iron Lead Lithium Magnesiium Manganese Molybdenum	Nickel Potassium Sodium Selenium Tin Strontium Titanium Thallium Zinc
Pesticides		
Chlordane (Technical) alpha – BHC beta – BHC delta – BHC gamma - BHC (Lindane) Heptachlor Aldrin	Heptachlor epoxide Endosulfan I Dieldrin 4, 4' – DDE Endrin Endrin ketone Endrin aldehyde	Endosulfan II 4, 4' – DDD Endosulfan sulfate 4, 4' – DDT Methoxychlor Toxaphene
Organophosphorus Pesticides		
Thionazin	Ethyl parathion	Tetraethyldithiopyro-phosphate
Polychlorinated Biphenyls (PCBs)		
Arochlor 1016 Arochlor 1221 Arochlor 1232	Arochlor 1242 Arochlor 1248	Arochlor 1254 Arochlor 1260

Table 2. Summary of Methods

Parameter	Analytical Method	Preparation Method
pH	SW846 9040	SW846 9040
Acidity (Titrimetric)	SM20 2310 B (4a)	
Alkalinity, Total	SM18 2320 B	SM18 2320 B
Amenable Cyanide	SM18 4500-CN E	SM18 4500-CN E
Biochemical Oxygen Demand	SM18 5210 B	SM18 5210 B
Bromide	MCAWW 300.1A	MCAWW 300.1A
Chemical Oxygen Demand	MCAWW 410.4	MCAWW 410.4
Chloride	MCAWW 300.1A	MCAWW 300.1A
Cyanide, Total	SW846 9012A	SW846 9012A
Dissolved Organic Carbon	SW846 7196A	SW846 7196A
Fluoride	MCAWW 300.1A	MCAWW 300.1A
Hexavalent Chromium	EPA 901.1 MOD	
Hardness, Total	SM20 2340C	
Mercury in Liquid Waste	SW846 7470A	SW846 7470A
N-Hexane Extractable Material	CFR136A 1664A H	EPA 1664A
Nitrate as N	MCAWW 300.1A	MCAWW 300.1A
Nitrite-Nitrate	MCAWW 353.2	MCAWW 353.2
Nitrite as N	MCAWW 300.1A	MCAWW 300.1A
Nitrogen, Ammonia	MCAWW 350.1	MCAWW 350.1
Organochlorine Pesticide	SW846 8081A	SW846 3510C
Organophosphorus Compounds	SW846 8141A	SW846 3510
Phenolics	SW846 9066	SW846 9066
Polychlorinated Biphenyls	SW846 8082	SW846 3510C
Semi volatile Organic Compounds	SW846 8270C	SW846 3520C
Specific Conductance	MCAWW 120.1	MCAWW 120.1
Sulfate	MCAWW 300.0A	MCAWW 300.0A
Sulfides, Total	SW846 9030B/903	SW846 9030B/903
Total Phosphorus	MCAWW 365.2	MCAWW 365.2
Total Dissolved Solids	SM18 2540 C	
Total Kjeldahl Nitrogen	MCAWW 351.3	MCAWW 351.3
Total Organic Carbon	SM20 5310B	
Total Suspended Solids	SM20 2540D	
Trace Inductively Coupled Plasma	SW846 6010B	SW846 3005A

Table 2. Summary of Methods		
Parameter	**Analytical Method**	**Preparation Method**
Metals	SW846 6010B	SW846 3010A
Trivalent Chromium	SW846 6010B	Wet None
Turbidity (Nephelometric)	MCAWW 180.1	MCAWW 180.1
Volatile Organics by GC/MS	SW846 8260B	SW846 5030B
Ethylene Glycol	SW846 8015	SW846 8015
Methylene Blue Activated Substances (MBAS)	SM5540C	SM5540C

Under the updated sampling plan, the following grab samples were collected at each of the volunteered locations:

- A supply water sample (before the blending of additives);
- One influent water sample following blending with fracturing additives, excluding sand;
- Flowback water samples collected on 1, 5 and 14 days after hydraulic fracturing; and
- Water from the producing well at 90 days after completion.

Following the collection of the samples and the performance of all of the determinations, the data was organized, qualified and tabulated by GTI.

RESULTS FROM THE MARCELLUS

Throughout the performance of the flowback water sampling program, natural gas development companies of the Marcellus Shale provided a high level of access to all of the host sites that was necessary to obtain the critical flowback water samples at the standardized times of 0, 1, 5, and 14 days following the hydraulic fracturing event of each host site well. About a third of the companies assisted with the collection of a 90 day sampling of the flowback water, as well. In total, 17 shale gas companies enabled the sampling of 19 locations within the Marcellus Shale Region, including 3 locations in West Virginia and 16 locations in Pennsylvania.

Flowback Water Collection Characteristics

Water volumes associated with 12 of the 19 wells sampled in this project are shown in Table 3. Of the 12 wells reporting water volume information, five wells were vertical wells and seven wells were of horizontal configuration. Of the vertical wells, an average of approximately 40,000 bbls of influent water were used to achieve fracturing, and about 15,000 bbls on average were collected within a 90 day period. Of the horizontal wells, an average of approximately 90,000 bbls of influent water were used to achieve fracturing, followed by a collection of about 16,000 bbls of effluent water (flowback). Cumulative volumes of water collected over time for these 12 completed wells are shown in Table 3.

Table 3: Water Use and Flowback Water Collection Associated with Hydraulic Fracturing Completion of Shale Gas Wells

Location	Well Type	Total Vol. Frac Fluid Used, bbls	Cumulative Volume of Flowback Water, BBL				Percent Collected
			1 Day*	5 Days	14 Days	90 Days	
A	Vertical	40,046	3,950	10,456	15,023		37.5
B	Vertical	94,216	1,095	10,782	13,718	17,890	19.0
C	Horizontal	146,226	3,308	9,652	15,991		10.9
D	Horizontal	21,144	2,854	8,077	9,938	11,185	52.9
E	Horizontal	53,500	8,560	20,330	24,610	25,680	48.0
F	Horizontal	77,995	3,272	10,830	12,331	17,413	22.3
G	Horizontal	123,921	1,219	7,493	12,471	18,677	15.1
H	Vertical	36,035	3,988	16,369	21,282	31,735	88.0
K	Horizontal	70,774	5,751	8,016	9,473		13.4
M	Horizontal	99,195	16,419	17,935	19,723		19.9
N	Vertical	11,435	2,432	2,759	3,043	3,535	30.9
O	Horizontal	96,706	5,131	19,202			19.8
Q	Vertical	23,593	1,315	3,577	5,090		21.6
S	Vertical	16,460	2,094	7,832	9,345	10,723	65.1
			Weighted Average % Collected ➔				24.3

* Days from the hydraulic fracturing event.

General Chemistry

A summary of the general chemical characteristics of the water influent streams and the flowback water effluents associated with the initiation of the fracing process are presented in Table 4. Raw Source water is compared against blended water containing conditioning chemicals (minus sand). Dissolved solids measurements for the influent waters used for hydraulic fracturing (with additives) had a median value of 735 mg/l, which is considered in the range of fresh surface water supplies. Oil and grease measurements had a median value of almost 30 mg/l with a range of 0.5 to 255 mg/l. Total organic carbon had a range of 5.6 to 1,260 mg/l with a median of 226 mg/l; elevated values in these measurements may be due to various degrees of blending of reused brine waters into frac job influent water supplies.

A summary of the same characteristics is tabulated for water supplies from 7 locations (F, H, I, J, L, M, S) in Table 5; information in this table provides an indication of the quality of influent water before the blending of additives. The data in this table indicates that water supplies had very low total organic carbon content (< 4 ppm), low biochemical oxygen demand (< 2 ppm) and non-detect levels of oils and greases; the values for these parameters are well within the ranges expected for normal surface waters and groundwater. Total dissolved solids ranged from 50 to 5,500 mg/l with a median value around 390 mg/l; the upper end of the range may be due to the varied degree of flowback water reuse that is employed at these sites.

The water is of relatively modest alkalinity with a median values of 85 – 120 mg/l, reflecting low carbonate concentrations which allow for very high levels of soluble calcium. High levels of calcium confer a very high hardness on the water as evidenced by median hardness values of 17,700 and 34,000 mg/l for the 5-day and 14-day sample sets, respectively. Cations are dominated by sodium and calcium in this water; anions are dominated by chloride. Levels of total organic carbon (TOC) in the flowback water samples at 5 and 14 days (with median values of 63 and 39 mg/l) are substantially lower (by about 75%) than the TOC of the blended influent water with additives; a possible reason for this is that the polyacrylamide friction reducers exert a TOC in the influent stream and are removed as water resides in the down-hole environment. The same observation is made in comparing biochemical oxygen demand (BOD) values in flowback water with the BOD of the influent water streams; in general, the BOD levels of the 5-day and 14-day flowback waters are less than half the influent BOD concentrations. The moderate levels of BOD in the influent waters may have resulted from carbonaceous algae growth in the source water or resulted from the biodegradable nature of the additives (e.g. polyacrylamide friction reducing compounds). The loss of friction reducing compounds due to adherence to surfaces downhole may be responsible for the lower BOD concentrations in flowback waters.

Results from Day 1 and Day 5 are presented in Table 5. Day 1 results, in general, show a huge range of values, indicating the rapid change in concentrations with initiation of flowback. By Day 5, most sites are demonstrating concentrations trending toward the maximum seen by Day 10 or 90. Two interesting observations concern TOC and BOD, both of which show a slight decrease from the initial blended water, to Day 1, to Day 5.

Results from Day 14 and Day 90 are presented in Table 6. Day 14 results, in general, show a large range of values, based on one sample from Site K that was generally less concentrated than the 5 Day sample. Day 90 results are from five sites only, and reflect the deviations associated with a relatively small sample size.

Salt concentrations in influent water and in flowback water generated over time from the 19 sampling locations are tabulated in Table 7. As shown in Table 7, influent water usually contains moderate to low concentrations of salts. Following the use of this water for hydraulic fracturing, a flowback water stream that is collected from the well exhibits increasing concentrations of salts with time.

Table 4. Summary of Chemical Characteristics of Water Used for Hydraulic Fracture

	Raw Source[1] Water		Blended[4] Frac Water		
Parameter	Range	Median	Range	Median	Units
pH	6.7-7.3	7.1	6.0 - 8.9	7.2	No Units
Acidity	< 5 – 5.5	< 5	< 5 - 1230	< 5	mg/l
Total Alkalinity	6.2 – 88.8	71.4	< 1 – 308	81.8	mg/l
Hardness as CaCO3	18 - 1,080	140	26 - 9,500	130.0	mg/l
Total Suspended Solids	<2 – 24	9.6	< 2 - 5,290	155.0	mg/l
Turbidity	1.3 – 33.7	4.3	2.7 – 715	249.0	NTU
Chloride	4.1 – 3,000	42.3	18 - 10,700	90.2	mg/l
Total Dissolved Solids[2]	51 – 5,510	390	221 - 27,800	735.0	mg/l
Specific Conductance	54.8 – 10,100	466	177 - 34,600	726.0	umhos/cm
Total Kjeldahl Nitrogen	< 2.3 – 56.4	2.2	2.3 – 400	33.5	mg/l
Ammonia Nitrogen	< 0.24 – 20.8	0.52	0.58 – 441	5.9	mg/l
Nitrate-Nitrite	< 0.01 – 3.0	0.51	< 0.032 - 0.34	0.1	mg/l
Nitrite as N	< 0.0032 – 4.9	< 0.0032	< 2.0 – 1740	271.0	mg/l
Biochemical Oxygen Demand	< 2.0 – 110	< 2.0	< 4.3 - 47,400	1730.0	mg/l
Chemical Oxygen Demand	< 4.3 – 924	18.4	5.6 - 1,260	226.0	mg/l
Total Organic Carbon (TOC)	1.8 – 202	3.8	5 - 1,270	301.0	mg/l
Dissolved Organic Carbon	1.4 – 222	3.2	< 0.49 – 255	29.2	mg/l
Oil & Grease (HEM)	-	< 0.5	< 1.7 – 680	4.6	mg/l
Cyanide, Total	< 1.7 – 625	< 1.7	< 0.005 - 0.87	< 0.005	µg/l
Amenable Cyanide	< 0.005 - 0.3	< 0.005	< 0.014 – 107	0.9	mg/l
Bromide	< 0.0014 – 1.9	0.14	< 0.004 - 58.3	0.004	mg/l
Fluoride	< 0.004 - 1.2	< 0.004	< 1.2 - 8.8	< 1.2	mg/l
Total Sulfide	1.2 - 5.6	1.6	< 0.031 – 2920	50.3	mg/l
Sulfate	3.8 – 139	43.7	< 0.03 – 16	0.14	mg/l
Total Phosphorus	< 0.03 – 0.1	0.044	< 0.0057 - 0.77	0.033	mg/l
Total Recoverable Phenolics	0.0057 - 0.14	0.0065	0.05 – 0.50	0.05	mg/l
Methylene Blue Active Substances (MBAS)[3]	0.05 – 0.50	0.05	6.0 - 8.9	7.2	mg/l

[1] Water Supplies at 7 Locations: F, H, I, J, L, M, S. [2] Upper end concentrations in the TDS range may be due to implementation of flowback water reuse and blending into the influent stream. [3] Data analysis for 8 Locations: D, F, H, I, J, M, N, S. [4] Additives included corrosion inhibitors, scale inhibitors, friction reducers, biocides, and oxygen scavengers. Blended water samples were taken before the addition of sand.

Table 5: Range of Results from 1 and 5 Day Samples

General Chemistry	Day 1		Day 5		
	Range	Median	Range	Median	Units
pH	5.9- 7.9	7.4	5.8- 7.2	6.6	No Units
Acidity	ND		5- 447	48.7	mg/l
Total Alkalinity	107- 577	251	48.8- 327	135	mg/l
Hardness as CaCO3	156- 25,000	4,150	5,100- 55,000	20,000	mg/l
Total Suspended Solids	6.8- 522	71	10.8- 3220	102	mg/l
Turbidity	10- 461	52.1	14- 1540	92	NTU
Chloride	64.2- 151,000	9,890	26,400- 148,000	43,900	mg/l
Total Dissolved Solids	680- 122,000	18,900	38,500- 238,000	72,700	mg/l
Specific Conductance	479 645,000	37,750	79,500- 470,000	175,000	umhos/cm
Total Kjeldahl Nitrogen	14.2- 158	52.9	38- 204	89.5	mg/l
Ammonia Nitrogen	2.8- 173	32	29.4- 242	90	mg/l
Nitrate-Nitrite	0.01- 2.8	0.5	0.049- 1.2	0.36	mg/l
Nitrite as N	ND- 6.7	3.1	4.8- 25.9	11.8	mg/l
Biochemical Oxygen Demand	27.6- 1,440	327.5	37.1- 1,950	141	mg/l
Chemical Oxygen Demand	397- 10,700	1,660	195- 17,700	4,845	mg/l
Total Organic Carbon	2.2- 672	142	3.7- 388	61.8	mg/l
Dissolved Organic Carbon	20.2- 657	253	30.7- 501	88.3	mg/l
Oil & Grease (HEM)	5.7- 53.9	13.7	0- 655	16.2	mg/l
Cyanide, Total	6.6- 177	21.5	5.2- 72.1	13.6	ug/L
Bromide	35.5- 376	120	0- 1190	445	mg/l
Fluoride	0.077- 32.9	0.975	0.045- 17.3	2.4	mg/l
Total Sulfide	1.6- 3.2	1.6	1.6- 5.6	2.4	mg/l
Sulfate	10.7- 348	46	2.4- 106	37.8	mg/l
Total Phosphorus	0.037- 21.8	0.18	0.053- 2.3	0.305	mg/l
Total Recoverable Phenolics	0.007- 0.064	0.027	0.0076- 0.31	0.024	mg/l

Table 6: Range of Results from 14 and 90 Day Samples

	Day 14 (17 Sites Reporting)		Day 90 (5 Sites Reporting)		
General Chemistry	Range	Median	Range	Median	Units
pH	4.9- 6.8	6.2	5.2- 6.2	5.9	No Units
Acidity	19.4- 473	114	162- 925	220	mg/l
Total Alkalinity	26.1- 121	85.2	7.5- 75.2	41.4	mg/l
Hardness as CaCO3	630- 95,000	34,000	40,000- 85,000	77,000	mg/l
Total Suspended Solids	17- 1150	209	150- 446	201	mg/l
Turbidity	10.5- 1090	233	106- 277	174	NTU
Chloride	1,670- 181,000	78,100	78,300- 185,000	122,000	mg/l
Total Dissolved Solids	3,010- 261,000	120,000	155,000- 345,000	216,000	mg/l
Specific Conductance	6,800- 570,000	256,000	249,000- 600,000	385,000	umhos/cm
Total Kjeldahl Nitrogen	5.6- 261	116	92.8- 312	136	mg/l
Ammonia Nitrogen	3.7- 359	121	96- 416	259	mg/l
Nitrate-Nitrite	0.025- 0.92	0.25	ND- 0.029	0.0145	mg/l
Nitrite as N	1.7- 77.4	18.75	42.8- 42.8	42.8	mg/l
Biochemical Oxygen Demand	2.8- 2070	39.8	4.1- 1080	33.6	mg/l
Chemical Oxygen Demand	228- 21,900	8530	2,630- 36,600	16,200	mg/l
Total Organic Carbon	1.2- 509	38.7	4- 5,680	117	mg/l
Dissolved Organic Carbon	5- 695	43	3.3- 5,960	117	mg/l
Oil & Grease (HEM)	7.4- 103	30.8	14.7- 62.6	21.3	0
Cyanide, Total	1.9- 7.4	5	42.6- 42.6	42.6	ug/L
Bromide	15.8- 1,600	704	766- 1,990	1,260	mg/l
Fluoride	ND 2		ND-		mg/l
Total Sulfide	1.6- 3.2	2	2.4- 4	3.2	mg/l
Sulfate	0.078- 89.3	40	83.8- 83.8	83.8	mg/l
Total Phosphorus	0.035- 2.2	0.115	ND		mg/l
Total Recoverable Phenolics	0.006- 0.31	0.016	0.0091- 0.23	0.0295	mg/l

Table 7: Concentration of Total Dissolved Solids in Flowback Water at 19 Locations, (mg/l)

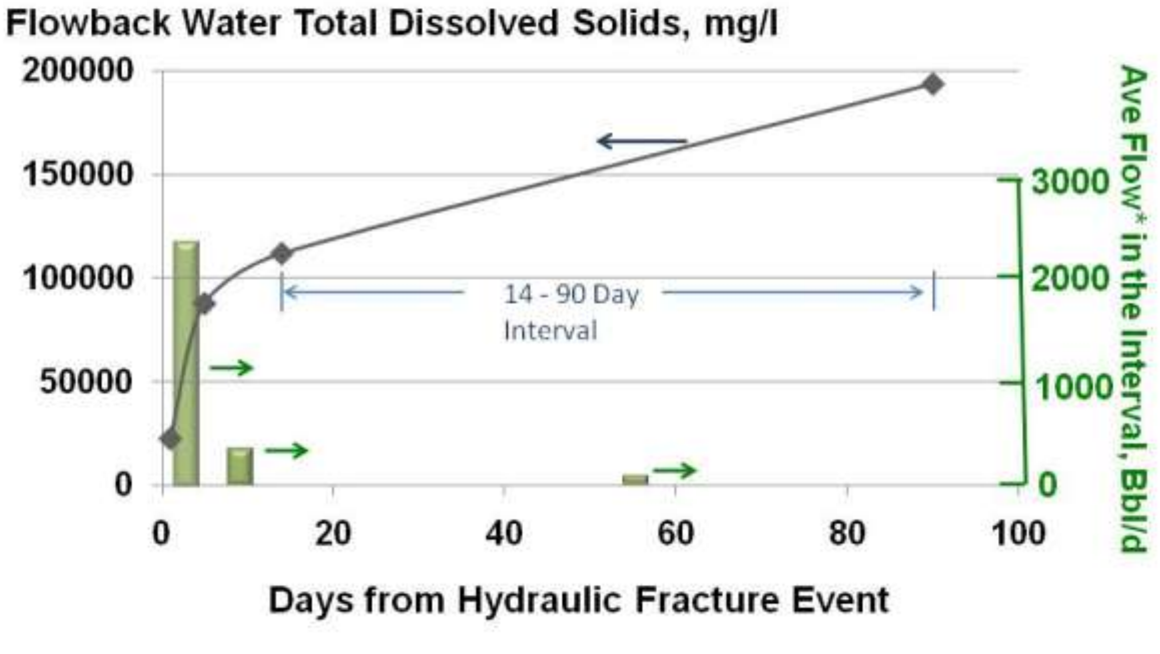
Location	Day 0*	Day 1	Day 5	Day 14	Day 90
A	990	15,400	54,800	105,000	216,000
B	27,800	22,400	87,800	112,000	194,000
C	719	24,700	61,900	110,000	267,000
D	1,410	9,020	40,700		155,000
E	5,910	28,900	55,100	124,000	
F	462	61,200	116,000	157,000	
G	1,920	74,600	125,000	169,000	
H	7,080	19,200	150,000	206,000	345,000
I	265	122,000	238,000	261,000	
J	4,840	5,090	48,700	19,100	
K	804	18,600	39,400	3,010	
L	221	20,400	72,700	109,000	
M	371			228,000	
N	735	31,800	116,000		
O	2,670	17,400	125,000	186,000	
P	401	11,600	78,600	63,900	
Q	311	16,600	38,500	120,000	
R	481	15,100	46,900	20,900	
S	280	680	58,300	124,000	

*Day 0 sample was taken of the influent water plus additives without sand.

A typical profile of salt concentrations (such as Location B) measured in flowback water with time is shown in Figure 1. Early flowback water emerging soon after the frac job is relatively low in TDS content. Following the initial day, the concentration of total dissolved solids increases with time from low salt concentrations to a plateau of elevated salt levels as measured at 14 and 90 days. Also shown in this diagram is the marked concomitant decrease in flowback brine flow with time, exhibiting a high initial flow rate of over 2,400 bbls/day, then decreasing to a minimal flow rate of less than 55 bbls/day after the initial few weeks following completion, a 98% reduction of daily flow.

The lowest flow rate bar shown on the chart in Figure 1 was calculated from cumulative water data between 14 and 90 days; actual flows in the 60 to 90 day period are significantly less than 55 bbls/day. The diagram, however, demonstrates that although the TDS levels in the flowback water emerging between 14 and 90 days almost doubles to nearly reach 200,000 mg/l. The daily brine volumes produced by the well decrease to a low rate that can be easily managed as a typical produced water stream.

Figure 1. Salt Concentration and Flowback Water Flow Versus Time from Location B



•Average Daily Flow of the Flowback Water Output within Each Interval

General characteristics of the samples tested in this project appear very consistent with the ranges of values reported in the literature for normal produced waters (USGS, 2004). The large database collected by the USGS indicates that salinities for produced waters generated among all basins can vary widely from approximately 5,000 to greater than 350,000 mg/l of total dissolved solids. Chloride is the dominant anion in nearly all formation waters associated with petroleum and with most conventional natural gas

(Kharaka and Rice, 2004). Sodium is the most dominant cation in most producing fields and constitutes 70 to more than 90% of total cations (USGS, 2004). General characterization data from the waters tested at the 19 locations of this project appear consistent with much of the available compositional information available from the USGS database. The USGS database containing produced water characterization data from more than 60,000 wells is accessible from the Internet at: http://energy.cr.usgs.gov/prov/prodwat/intro.htm .

Total organic carbon reflects a trend generally opposite that of the total dissolved solids. Table 8 shows that the TOC in the flowback water typically decreases over time. The BOD (Table 9) is more erratic. Some wells remain constant over time, while other wells increase; still others decrease in measured BOD with time.

Table 8: Total Organic Carbon TOC (mg/l)

Site	Day 0	Day 1	Day 5	Day 14
A	350	260	NS	38.7
B	168	207	50.6	34.2
C	167	82.5	32.9	14.4
D	741	342	161	NS
E	226	108	46.2	5.9
F	205	43.5	62.8	44
G	123	60.8	42.2	NS
H	78.3	1260	443	119
I	607	610	48	12.8
J	569	56.6	27.5	23.6
K	949	124	103	7.2
L	202	155	115	80.5
M	86.6	2.2	3.7	1.2
N	208	28.1	37.8	NS
O	575	308	237	509
P	5.6	292	287	226
Q	410	142	46.5	24
R	173	604	388	323
S	931	672	104	150
Median	208	155	57	36
Average	357	282	124	101

Table 9: Biochemical Oxygen Demand (BOD mg/l)				
Site	Day 0	Day 1	Day 5	Day 14
A	794	353		3
B	ND	132	1,950	149
C	5	132	63.7	39.8
D	438	656	721	NS
E	788	158	106	32.4
F	154	75.4	64.8	120
G	302	144	7.3	NS
H	110	1,740	737	138
I	578	399	99	10.4
J	47	43	48	20.3
K	430	650	214	30.5
L	ND	ND	27.6	37
M	137	36.3	103	10
N	166	73.2	70.9	NS
O	924	606	1,520	725
P	4	391	1,260	752
Q	121	184	144	98.1
R	271	692	1250	6
S	2,220	1,440	218	990
Median	271	269	106	38
Average	441	439	453	198

Organic Compounds

The organic compounds included in the characterization of water samples included the categories of volatile organics, semi volatile organics, chlorinated pesticides, organophosphorus pesticides, and polychlorinated biphenyls. Most of the compounds in the first two categories and all compounds in the last three categories were included on the list of analyses in response to recommendations from PA-DEP and WV-DEP. The following sections summarize the results among all five of the categories of analysis.

Volatile Compounds

Samples collected from Locations A through S were analyzed for 70 volatile compounds of highly varied chemical characteristics, including the volatile hydrocarbon constituents that are normally found in produced water (such as benzene, toluene, ethylbenzene, and xylenes – or BTEX, and naphthalene) as well as constituents not known to be associated with conventional produced water such as chlorinated solvents and halogenated aromatics.

Source water data (Day 0 minus sand) are presented in Table 10. Of 1330 measurements, only 92 observations of volatile compounds were made. Acetone was measured in 12 samples, representing the use of acetone as a component of the additives. BTEX and alkylated benzene isomers likely represent a component of water reuse from previous sites. Traces of halogenated solvents occasionally occur at the part per billion level. Apparently, the additives used in the fracking process do not manifest themselves amongst the most problematic volatile components.

As noted before, the organic components, unlike total salts, do not follow a timed based profile. In general, their appearance in the flowback waters appears anywhere from low and constant or intermittent and random. As such, the best means of presenting the volatile data for the 19 sites is to present tablulated distributions, ie., the number of observations within a stated concentration range. Table 11 shows the distribution of observations for all 60 samples. As an example, p-Isopropyltoluene was observed once at a concentration between 50-99 μg/l, twice between 10-49 μg/l, once between 1-4.9 μg/l, and undetected (ND) in 56 samples. Many of the compounds were observed only once in sixty samples, making them either incidental or mistaken. No compound was encountered in all sixty samples. The chemical most likely to be observed was acetone in 48 of sixty samples. Thirty five of the compounds from the voilatiles list were never observed. In total, 4200 measurements were taken and 3710 of them were "non-detects."

Table 10: Influent Water Day 0 (minus sand)

Volatiles	Observations	Range, µg/l	Median, µg/l
Naphthalene	7	0.55- 820	3.8
n – Propylbenzene	1	ND- 2	
1, 2, 4 – Trimethylbenzene	10	0.72- 140	9.15
1, 3, 5 – Trimethylbenzene	7	2.8- 100	7.7
Isopropylbenzene	2	0.95- 0.95	0.95
2 – Butanone	2	3.6- 7.5	5.55
Xylenes (total)	11	2.6- 210	18
sec – Butylbenzene	2	3.2- 84	43.6
Acetone	12	5.4- 170	17.5
Benzene	4	2.2- 6.7	6.7
Bromodichloromethane	1	ND- 2	
Bromoform	4	7.8- 9.3	8.55
Carbon disulfide	4	1.6- 54,000	12,250
Chloroform	1	ND- 2.4	
Dibromochloromethane	1	ND- 2.1	
1, 2 – Dichloroethane	1	ND 2.6	
Ethylbenzene	5	0.81- 19	1.7
Methylene chloride	1	ND- 13	
Tetrachloroethene	2	1.3- 1.4	
Toluene	13	0.93- 81	5.6
Trichloroethene	1	ND- 0.81	
Total Observations	92	of 1330	Measurements

Constituents that exceeded 100 ppb included components that are commonly present in conventional produced water, such as naphthalene, BTEX, several methylated benzene compounds and an alkylated toluene (p-isopropyltoluene). Few determinations of these compounds exceeded 1 ppm and only one occurrence was above 2 ppm. In the locations where BTEX was measured at levels above 100 ppb, BTEX levels in the 5-day and 14-day flowback waters that were in contact with the natural gas producing formation were generally higher than BTEX concentrations in the influent water streams, indicating that these compounds are naturally occurring and not the result of additives. Levels of BTEX and methylated aromatics vary from location to location. Determination of factors that control levels of these compounds could potentially be determined through a correlation of the composition of volatiles and other flowback water characteristics with the key shale gas development parameters of geographic area, depth of wells, completion methods, etc. For a distribution of all volatile organic concentration observations, see Figure 2.

Table 11: Number of Observations of 70 Volatile Compounds in All 60 Marcellus Samples

Number of Observations Between Limits in µg/l	>1000	500-999	100-499	50-99	10-49	5-9.9	1-4.9	ND-1	ND
p – Isopropyltoluene	0	0	0	1	2	0	1	0	56
Naphthalene	0	2	1	0	2	0	8	3	44
n – Propylbenzene	0	0	0	1	0	0	1	0	58
1, 2, 3 – Trichlorobenzene	0	0	0	0	1	1	0	0	58
1, 2, 4 – Trichlorobenzene	0	0	0	0	0	0	1	0	59
1, 2, 4 – Trimethylbenzene	0	4	1	5	8	2	14	5	21
1, 3, 5 – Trimethylbenzene	0	3	2	1	7	6	7	2	32
Isopropylbenzene	0	0	2	1	0	0	2	2	53
2 – Butanone	0	0	0	0	2	2	1	0	55
Xylenes (total)	4	1	8	0	8	7	7	0	25
n - Butylbenzene	0	0	0	0	0	0	1	0	59
sec - Butylbenzene	0	0	0	2	0	0	0	0	58
Acetone	4	1	9	2	26	5	0	0	12
Acrylonitrile	0	0	0	0	0	1	0	0	59
Benzene	3	1	7	1	2	7	7	1	31
Bromoform	0	0	0	0	0	1	0	0	59
Bromomethane	0	0	1	0	0	0	0	0	59
Carbon disulfide	2	0	2	0	1	0	0	0	55
Chloroform	0	0	0	0	1	0	1	0	58
Chloromethane	0	0	1	0	0	1	1	0	57
Ethylbenzene	0	1	4	1	6	1	5	3	39
Methylene chloride	0	0	0	0	0	1	2	0	57
4 - Methyl - 2 - pentanone (MIBK)	0	0	0	0	0	0	0	1	59
Styrene	0	0	0	0	0	0	1	0	59
Tetrachloroethene	0	0	0	0	0	1	0	0	59
Toluene	5	4	4	2	3	2	19	2	19
All 35 Others (See Table 1)	0	0	0	0	0	0	0	0	2450
Total	18	17	42	17	69	38	79	19	3710

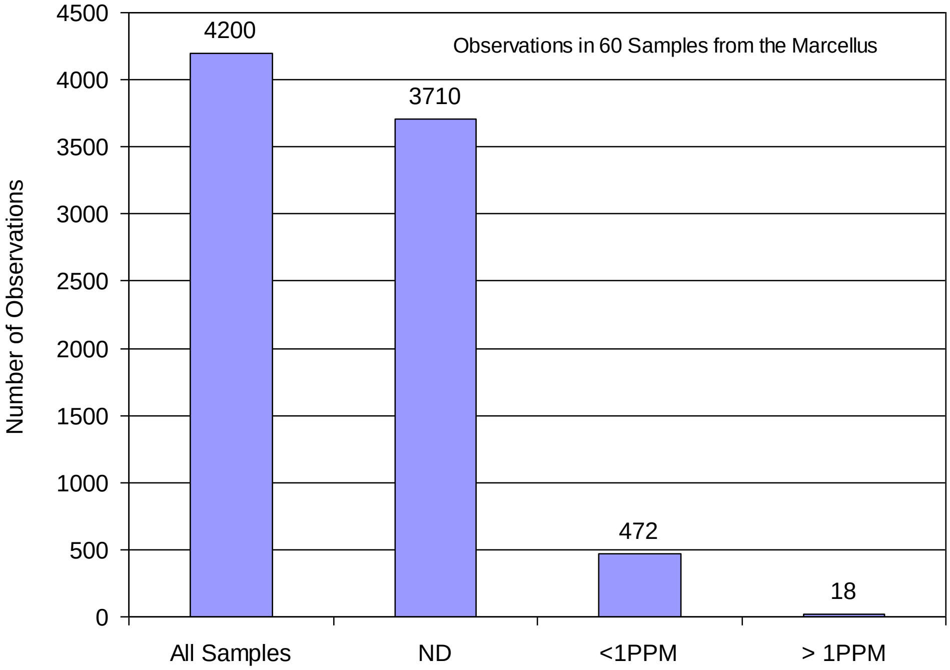


Figure 2: Distribution of Observations for 70 Volatile Organics from 60 Samples from the Marcellus

Semi volatile Compounds

A total of 112 semi volatile organic compounds (as listed in Table 1) were included in the analysis of influent water and in flowback water samples. A summary of the results of semi volatile determinations in these samples the day 0 source water (chemical additives minus sand) is presented in Table 12. The most commonly encountered semi volatiles belong to the phthalate ester group, probably representing introduced plasticizers. Pyridine is commonly encountered and possibly represents a residue from some of the manufacture of some of the additives. Occasional traces of PAH's are present, likely from water reuse in some of the input waters. In a total of 19 samples, a total of 2204 chemical tests were performed. Only 76 samples were above appears to not appreciably influence the concentrations of the 116 listed semi volatile organics.

Table 12: Semi-Volatile Content in 19 Marcellus Influent Samples

Source Water Day 0	Observations In 19 Samples	Range, µg/l		Median of Observation
Acetophenone	1	ND-	0.97	
Benzo (a) anthracene	1	ND-	1.1	
Benzo (a) pyrene	1	ND-	6.9	
Benzo (b) fluoranthene	1	ND-	11	
Benzo (ghi) perylene	1	ND-	7.4	
Benzo (k) fluoranthene	1	ND-	6.7	6.7
Benzyl alcohol	2	74-	74	74
bis (2 - Chloroethyl) - ether	1	ND-	4300	
bis (2 - Ethylhexyl) phthalate	11	2-	21	9.4
Butyl benzyl phthalate	1	ND-	5.1	
Chrysene	1	1.7-	1.7	1.7
Dibenz (a, h) anthracene	1	ND-	12	12
Di - n butyl phthalate	9	0.29-	1.7	0.6
1, 2 - Dichlorobenzene	1	ND-	0.68	
1, 4 - Dichlorobenzene	1	ND-	0.6	
2, 6 - Dichlorophenol	1	ND-	2	
Diethyl phthalate	2	0.49-	1.8	1.145
2, 4 - Dimethylphenol	1	ND-	0.39	
Fluoranthene	1	ND-	5.5	
Fluorene	2	0.83-	1.2	1.015
Indeno (1, 2, 3 - cd) pyrene	2	10-	10	10
2 - Methylnaphthalene	7	1.3-	300	7.5
Naphthalene	6	0.61-	1800	4.3
Phenanthrene	7	0.28-	24	1.3
2 - Picoline	1	ND-	5.3	
Pyrene	3	0.19-	0.54	0.22
Pyridine	9	0.91-	510	17
All 89 Other Chemicals (Table 1)	0	ND		ND

For all sample times, semi-volatile compound determinations that were detectable are listed in Table 13. As seen in this table, only four constituents were measured in any of the samples at levels exceeding 10 ppb. Acetophenone and aniline are commonly associated with fossil fuels, as are the methylated phenols. The only compound that was measured above 1 ppm was pyridine. Pyridine is a nucleophile used widely in the manufacture of certain chemicals and pharmaceuticals. Its presence may be due to its use as a precursor in the manufacture of one of the hydraulic fracturing additives. Most the semi volatile determinations were either non-detect (> 96% of the measurements) or at low trace levels (Figure 3). Most of the chemicals in Table 13 appeared as chance encounters, ie., detection in one or two of sixty samples.

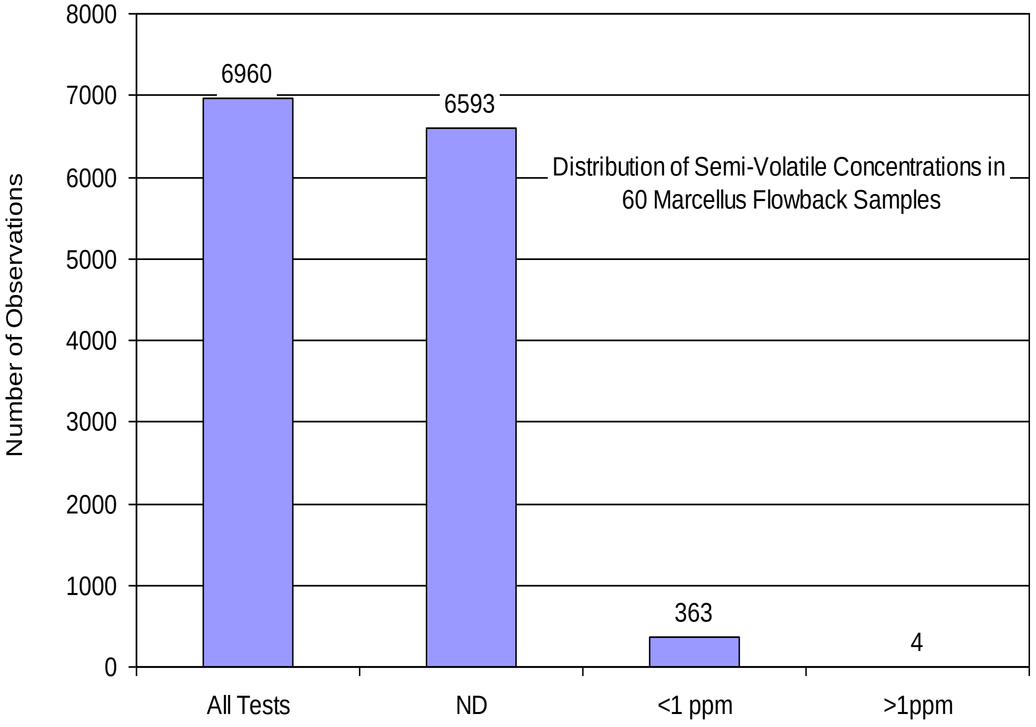


Figure 3: Distribution of Observations of Semi-Volatiles in 60 Marcellus Flowback Samples from 19 Sites

Table 13: Number of Observations of 116 Semi- Volatile Compounds in all 60 Marcellus Samples

Number of Observations Between Limits in µg/l	>1000	500-999	100-499	50-99	10-49	5-9.9	1-4.9	ND-0.99	ND
Diphenylamine	0	0	0	0	0	0	2	0	58
1, 4 – Dioxane	1	0	0	0	15	9	4	2	29
Acenaphthene	0	0	0	0	0	0	0	3	57
Acenaphthylene	0	0	0	0	0	0	0	1	59
Acetophenone	0	0	0	0	6	3	6	9	36
Aniline	0	0	0	0	0	0	2	0	58
Benzo (a) anthracene	0	0	0	0	0	0	2	0	58
Benzo (a) pyrene	0	0	0	0	0	0	2	0	58
Benzo (b) fluoranthene	0	0	0	0	0	0	2	0	58
Benzo (ghi) perylene	0	0	0	0	0	0	3	0	57
Benzo (k) fluoranthene	0	0	0	0	0	0	1	1	58
Benzyl alcohol	0	0	1	0	2	3	1	0	53
bis (2 - Chloroethyl) - ether	0	0	0	0	1	0	0	0	59
bis (2 - Ethylhexyl) phthalate	0	2	0	0	8	9	15	1	25
Butyl benzyl phthalate	0	0	0	0	1	3	0	0	56
Chrysene	0	0	0	0	0	0	2	0	58
Dibenz (a, h) anthracene	0	0	0	0	0	0	2	0	58
Di - n butyl phthalate	0	0	1	1	3	2	5	10	38
1, 2 - Dichlorobenzene	0	0	0	0	0	0	0	2	58
1, 3 - Dichlorobenzene	0	0	0	0	0	0	0	1	59
1, 4 - Dichlorobenzene	0	0	0	0	0	0	0	2	58
Diethyl phthalate	0	0	0	0	1	0	8	4	47
2, 4 - Dimethylphenol	0	0	0	0	3	4	1	2	50
Dimethyl phthalate	0	0	0	0	0	1	0	0	59
Di - n - octyl phthalate	0	0	0	0	2	3	3	0	52
Disulfoton	0	0	0	0	0	0	1	0	59
Ethyl methanesulfonate	0	0	0	0	0	0	0	0	60
Fluoranthene	0	0	0	0	0	5	2	0	53
Fluorene	0	0	0	0	0	2	2	8	48
Hexachlorobenzene	0	0	0	0	0	0	1	1	58
Indeno (1, 2, 3 - cd) pyrene	0	0	0	0	0	0	2	0	58
2 - Methylnaphthalene	0	0	3	2	0	0	9	6	40
2 – Methylphenol	0	0	0	0	3	6	2	3	46
3 - Methylphenol & 4 - Methylphenol	0	0	0	0	7	3	3	13	34
Naphthalene	1	1	0	0	3	1	5	5	44
4 – Nitroaniline	0	0	0	0	0	0	1	0	59
N - Nitrosodiphenylamine	0	0	0	0	0	0	1	0	59
Phenanthrene	0	0	0	0	2	0	5	7	46
Phenol	0	0	0	0	5	0	4	2	49
2 – Picoline	0	0	0	0	1	0	1	0	58
Pyrene	0	0	0	0	1	0	3	5	51
Pyridine	2	2	21	4	5	3	6	0	17
1, 2, 4 - Trichlorobenzene	0	0	0	0	0	0	0	2	58
All 74 Others (See Table 1)	0	0	0	0	0	0	0	0	4440
Total	4	5	26	7	69	57	109	90	6593

Pesticides

Determinations of the 20 chlorinated pesticides and three organophosphorus pesticides listed in Table 1 were conducted on the influent and 14-day flowback water streams. None of these pesticides were detected. This would suggest that no chlorinated pesticides were introduced with the additives with the influent water during well completions.

Polychlorinated Biphenyls (PCBs)

Determinations of the 7 polychlorinated biphenyl compounds (arochlors) listed in Table 1 were conducted on the influent and 14-day flowback water streams. Results from the measurements of organophosphorus pesticides in all samples of the influent water and in the 14-day flowback water are summarized in Figures 16 and 17, respectively. As seen from these graphs, all determinations for PCBs were measured as non-detect. This would suggest that no PCBs were introduced with the additives with the influent water during well completions.

Metals

Total metals data for the six raw water samples and the 19 influent water samples with additives are presented in Table 14. For the most part, the differences in the ranges of concentration between the two sample sets can be explained by the differences expected for the different population (6 vs 19 samples). There is an added unknown statistical bias in the subset of the number of samples in the influent utilizing blended (reused) water versus the number of raw water sources utilizing reused water.

Table 14: Metals Data in Raw Water and Source Water with Additives

All units mg/l	Raw Water day 0 6 Samples				Influent with Additives 19 Samples			
	Obs	Range		Median	Obs	Range		Median
Aluminum	4	0.122-	0.264	0.213	5	0.177-	2	0.4
Antimony	2	0.0146-	0.0154	0.015	1	0.015-	0.0154	0.0154
Arsenic	0				0			
Barium	6	0.243-	5.48	0.589	6	0.108-	87.1	1.005
Beryllium	0				0			
Boron	5	0.0189-	2.45	0.0343	5	0.019-	2.58	0.0433
Calcium	6	4.88-	40.1	31.75	6	6.69-	241	32.2
Cadmium	1	0.0017-	0.0017	0.0017	1	0.002-	0.0017	0.0017
Cobalt	0	ND			0	ND		
Chromium	0	ND			0	ND		
Trivalent		ND				ND		
Chromium	0				0			
Copper	0	ND			1	0.045-	0.0445	0.0445
Iron	6	0.192-	4.31	0.4995	6	0.137-	3.56	0.4455
Lead	0	ND			0	ND		
Lithium	3	0.0338-	2.24	0.0422	3	0.03-	2.34	2.05
Magnesiium	6	1.08-	183	5.845	6	1.25-	183	13.87
Manganese	6	0.0087-	0.237	0.0817	5	0.008-	0.395	0.127
Molybdenum	0	ND			0	ND		
Nickel	1	ND-	0.0111	0.0111	1	0.02-	0.0195	0.0195
Potassium	4	2.36-	53.6	2.89	4	2.25-	57.4	7.265
Sodium	6	4.2-	1380	31.05	6	32.6-	1460	59.5
Selenium	0	ND-			1	0.035-	0.0353	0.0353
Tin	0	ND-			0	ND		
Strontium	6	0.352-	76.2	0.6785	6	0.206-	78.5	0.919
Titanium	1	ND-	0.0299	0.0299	2	0.019-	0.0271	0.0233
Thallium	0	ND			0	ND		
Zinc	6	0.0257-	0.172	0.0486	6	0.035-	0.176	0.0635
Mercury	3	5E-05-	0.00061	5E-05	3	4E-05-	6E-05	5E-05

Metals data, especially the top five cations, sodum, barium, iron, strontium and magnesium, tend to follow a timed profile. These data are presented by collection day to better show the trends. Summary data for days 1 and 5 are presented in Table 15. Summary data for days 14 and 90 are presented in Table 16. The 90 day data present a much smaller database (5 sites compared to 17-19 samples in the other sets). The top six metal ions in flowback water are sodium, calcium, magnesium, strontium and iron and potassium. These ions, and most others listed, increase from day 1 to day 90 and represent a significant increase over the raw water and influent water data in the Table 14.

Table 15: Metals Data for Marcellus Flowback Days 1 and 5

	Day 1 (19 Samples)				Day 5 (18 Samples)			
Metals (mg/l)	Obs	Range		Median	Obs	Range		Median
Aluminum	17	0.165-	4.03	0.507	17	0.111-	47.2	0.378
Antimony	13	0.0089-	0.0378	0.0247	10	0.017-	0.0472	0.0325
Arsenic	12	0.0133-	0.0551	0.0333	11	0.014-	0.124	0.043
Barium	19	0.332-	1450	37.6	18	21.4-	13900	736.5
Beryllium	0				0			
Boron	19	0.0181-	13.1	6.68	18	3.14-	97.9	12.05
Calcium	19	35.2-	19700	833	18	1440-	23500	5555
Cadmium	4	0.0002-	0.0029	0.00235	7	0.002-	0.0096	0.0038
Cobalt	3	0.0045-	0.0105	0.0057	0			
Chromium Trivalent	16	0.0075-	0.359	0.0318	14	0.008-	0.152	0.0271
Chromium	6	0.0075-	0.0491	0.0293	9	0.0075-	0.0924	0.0272
Copper	11	0.0096-	0.255	0.0571	9	0.029-	4.15	0.0789
Iron	19	2.68-	67.2	13.9	18	20.4-	180	41.25
Lead	12	0.0017-	0.0709	0.02565	8	0.021-	0.606	0.05605
Lithium	18	4.06-	129	14.05	18	10.6-	153	42.75
Magnesiium	19	16-	1320	89	18	135-	1550	581.5
Manganese	19	0.146-	5.96	0.782	18	0.881-	7.04	2.64
Molybdenum	19	0.0089-	0.372	0.0356	15	0.009-	0.147	0.0317
Nickel	17	0.0106-	0.203	0.0286	6	0.011-	0.187	0.02275
Potassium	19	2.69-	923	109	18	48.9-	2430	300.5
Sodium	19	63.8-	34700	6290	18	10700-	65100	18100
Selenium	1	ND-	0.0043	0.0043	0			
Tin	3	0.0038-	0.007	0.0051	1	ND-	0.026	0.0257
Strontium	19	0.58-	4330	167	18	345-	4830	1160
Titanium	11	0.0151-	0.092	0.0385	9	0.024-	0.313	0.107
Thallium	3	0.0049-	0.0272	0.0054	3	0.019-	0.0246	0.0194
Zinc	18	0.0561-	0.665	0.191	18	0.068-	1.23	0.164
Mercury	6	4E-05-	0.000074	5.05E-05	5	2E-05-	0.00024	0.000043

Table 16: Metals Data for Marcellus Flowback Days 14 and 90

	Day 14 with 17 Sites Reporting				Day 90 with 5 Sites Reporting			
Metals (mg/l)	Obs	Range		Median	Obs	Range		Median
Aluminum	15	0.158-	4.68	0.835	5	0.173-	1.04	0.37
Antimony	8	0.0092-	0.0491	0.02645	0			
Arsenic	12	0.0126-	0.135	0.07695	4	0.0462-	0.114	0.0726
Barium	17	0.0631-	12500	589	5	133-	4220	1440
Beryllium	2	0.00021-	0.0022	0.001205	0			
Boron	17	0.464-	114	13.6	5	13-	145	25.3
Calcium	17	14.3-	140000	9600	5	8500-	24000	18300
Cadmium	12	0.0014-	0.0124	0.00385	4	0.0025-	0.0077	0.00255
Cobalt	2	0.0109-	0.0278	0.01935	0			
Chromium Trivalent	15	0.0012-	0.567	0.0312	3	0.0135-	0.0209	0.0177
Chromium	10	0.0012-	0.0942	0.01335	1	ND-	0.0175	0.0175
Copper	11	0.0077-	0.518	0.079	2	0.0272-	0.0515	0.03935
Iron	17	0.439-	574	73.2	5	69.7-	158	93
Lead	10	0.0033-	0.596	0.092	3	0.0456-	0.97	0.068
Lithium	17	0.0077-	201	73.7	5	44.5-	137	88.6
Magnesiium	17	2.83-	1800	794	5	933-	1790	1710
Manganese	17	0.0587-	18.6	4.79	5	2.13-	9.77	4.72
Molybdenum	11	0.0066-	0.188	0.0324	1	0.017-	0.017	0.017
Nickel	8	0.0013-	0.769	0.05795	0			
Potassium	17	8.23-	2820	368	5	191-	3950	548
Sodium	17	70.7-	85600	31500	5	26900-	75800	39700
Selenium	4	0.0301-	0.0956	0.0367	1	ND-	0.044	
Tin	4	0.0039-	0.0235	0.02185	0			
Strontium	17	0.103-	5570	1850	5	1220-	8020	3480
Titanium	10	0.0636-	0.247	0.1435	4	0.13-	0.242	0.173
Thallium	2	0.0339-	0.151	0.09245	1	0.168-	0.168	0.168
Zinc	16	0.0117-	2.29	0.226	5	0.0293-	0.811	0.178
Mercury	2	0.000049-	0.00029	0.00017	1	ND-	0.000068	

RESULTS FROM THE BARNETT

Using the same protocols employed in the Marcellus, five sites were sampled in the Barnett. Flowback water samples were collected at the time intervals indicated in Table 17. Initial raw water for Sites LPG1 and LPG2 was from the same source and is represented by a single sample. Initial raw water for Sites LPG 3, LPG 4, and LPG5 was from the same source and is represented as a single sample. Four of five sites reported data on Day 1. Three sites reported on Day 5 and one site reported on Day 6. These four samples dates are treated together in discussions of Day 5-6 events. Three sites reported on Day 10 and one site reported on Day 12. These sample dates are treated together in discussions of Day 10-12 events. Sampling and assurance plans followed those developed for the Marcellus in Appendices A and B. Chemical results were collected and treated as described in Tables 1 and 2. Results from all samples taken from Sites LPG 1-5 are presented with the analysis results from the Marcellus in the GTI Flowback Water Information Base in Excel Format that was submitted by GTI to RPSEA.

Table 17: Sample Dates (Days after Fracture) for 5 Sites in the Barnett

	Day 0	Day1	Day 3	Day 5	Day 6	Day 7	Day 10	Day 12
LPG1	🟧	X	X	X			X	
LPG2	🟧	X	X	X			X	
LPG3	🟩	X		X		X		X
LPG4	🟩		X		X		X	
LPG 5	🟩	X						

Flowback Water Collection Volumes

Flowback volumes for Sites LPG1-4 were recorded on a daily basis. Selected points are presented in Table 18 to correspond with the chemical data presented the following sections. Data are similar in form to those presented for the Marcellus in Table 3. Like the Marcellus, water recovery is rapid during the first few days, with recovery rates slowing by day 10-12 after fracture.

Table 18: Cumulative Flow (BBL) for 5 Sites in the Barnett

Initial Fracture (BBL)		Recovered Volumes (Cumulative) BBL						
		Day1	Day 3	Day 5	Day 6	Day 7	Day 10	Day 12
LPG1	129,336	2,402	7,566	11,806	12,752	14,154	20,346	23,082
LPG2	127,076	957	3,256	5,175	6,171	7,146	10,031	11,878
LPG3	100,611	4,117	8,071	13,735	14,827	15,972	19,021	20,960
LPG4	155,362	873	2,878	3,986	4,274	4,522	5,209	5,745
LPG5	X	X	X	X	X	X	X	X

General Chemistry

A summary of the general chemical characteristics of the two water influent samples and the flowback water effluents associated with the completion and operation of wells of the 5 sampling locations are presented in Tables 19-22. Characteristics of the two samples of raw influent water are shown in Table 19. The pH of these streams ranging from 7.7 to 8.5 seems to be normal for surface waters. Dissolved solids measurements for the influent waters used for hydraulic fracturing (with additives) had a range of 200-800 mg/l, which is considered in the range of fresh surface water supplies. Interestingly, oil and grease measurements had a range of 17-22 mg/l and total organic carbon had a range of 124-143 mg/l; elevated values in these measurements may be due to various degrees of blending of reused waters into frac job influent water supplies.

Table 19. Summary of Chemical Characteristics of Influent Water Used for Hydraulic Fracturing after Additives were Blended

General Chemistry	LPG 3,4,5	LPG 1,2	Average	Units
pH	7.7	8.5		No Units
Acidity	ND	ND	ND	mg/L
Total Alkalinity	251	236	243.5	mg/L
Hardness as CaCO3	28	100	64	mg/L
Total Suspended Solids	360	80	220	mg/L
Turbidity	265	116	190.5	NTU
Chloride	151	21.6	86.3	mg/L
Total Dissolved Solids	800	203	501.5	mg/L
Specific Conductance	1550	484	1017	umhos/cm
Total Kjeldahl Nitrogen	36	21.9	28.95	mg/L
Ammonia Nitrogen	3.9	8	5.95	mg/L
Nitrate-Nitrite	0.048	0.036	0.042	mg/L
Nitrite as N	0.57	0.14	0.355	mg/L
Biochemical Oxygen Demand	130	245	187.5	mg/L
Chemical Oxygen Demand	829	559	694	mg/L
Total Organic Carbon (TOC)	143	124	133.5	mg/L
Dissolved Organic Carbon	84.3	281	182.65	mg/L
Oil & Grease (HEM)	22.2	17	19.6	mg/L
Cyanide, Total	ND	1.9	1.9	mg/L
Amenable Cyanide	ND	ND	ND	mg/L
Bromide	0.7	ND	0.7	mg/L
Fluoride	1.00	0.096	0.548	mg/L
Total Sulfide	ND	ND	ND	mg/L
Sulfate	107	28	67.5	mg/L
Total Phosphorus	3	0.11	1.555	mg/L
Total Recoverable Phenolics	ND	0.014	0.014	mg/L

Characteristics of flowback water sampled at 1 day, 3 days, 5-6 days, and 10-12 days following the hydraulic fracturing event are presented in Tables 20 and 21. The water is elevated in alkalinity with median values ranging from 725-1,200 mg/l. The water remains imbalanced with high levels of calcium and magnesium. Cations are dominated by sodium and calcium in this water. Anions are dominated by chloride. However, there is a fairly large sulfate component to the anionic balance, which has importance in the relative value of barium and strontium in the water. This topic is evaluated further in the discussion section.

Table 20 General Chemical Parameters, Barnett Day 1 and Day 3

General Chemistry Parameter	LPG1,2,3,5 Day 1			LPG 1,2,4 Day 3			
	Range		Median	Range		Median	Units
pH	6.7 -	8	7.2	6.5-	7.2	6.6	No Units
Acidity	ND-	ND	ND	ND-	ND	ND	mg/L
Total Alkalinity	482-	1,590	980	236-	1,550	1,340	mg/L
Hardness as CaCO3	840-	2,800	2,200	3,000-	24,000	4,600	mg/L
Total Suspended Solids	48-	237	153	59-	120	89	mg/L
Turbidity	37-	266	130	104-	371	154	NTU
Chloride	3,330-	17,900	11,405	17,500-	49,000	21,400	mg/L
Total Dissolved Solids	5,850-	31,400	25,050	33,500-	96,900	37,200	mg/L
Specific Conductance	11,300-	59,000	55,550	71,400-	174,000	82,600	umhos/cm
Total Kjeldahl Nitrogen	16-	203	155	74-	239	215	mg/L
Ammonia Nitrogen	9-	223	186	143-	309	251	mg/L
Nitrate-Nitrite	0.024-	0.024	0.024	0.051-	0.051	0.051	mg/L
Nitrite as N	81.9-	107	94.45	85.7-	96.8	91.25	mg/L
Biochemical Oxygen Demand	89-	1,480	311	94-	290	244	mg/L
Chemical Oxygen Demand	850-	4,280	1,485	1,900-	5,850	2,290	mg/L
Total Organic Carbon (TOC)	34.7-	99.1	47.5	15.4-	19	17.4	mg/L
Dissolved Organic Carbon	30.6-	91.3	53.55	9.7-	23.2	17.6	mg/L
Oil & Grease (HEM)	5.6-	1720	862.8	26.7-	26.7	26.7	mg/L
Cyanide, Total	15.6-	15.6	15.6	ND-	ND	ND	ug/L
Amenable Cyanide	ND-	ND	ND	ND-	ND	ND	mg/L
Hexavalent Chromium	0.014-	0.16	0.0165	0.011-	0.042	0.02	mg/L
Dissolved Hexavalent Chromium	0.01-	0.08	0.03	ND-	0.15	0.08	mg/L
Bromide	34.3-	532	303.5	270-	448	399	mg/L
Fluoride	1.6-	30.6	4.75	4-	4.9	4.45	mg/L
Total Sulfide	ND-	ND	ND	ND-	ND	ND	mg/L
Sulfate	259-	972	669	277-	1,010	585	mg/L
Total Phosphorus	0.37-	3.4	0.79	0.39-	0.66	0.525	mg/L
Total Recoverable Phenolics	0.034-	0.45	0.08	0.046-	0.13	0.088	mg/L

Table 21: Summary of General Chemistry of Flowback Water Days 5-6 and 10-12

General Chemistry	LPG 1,2,3,4 Day 5-6			LPG 1,2,3,4 Day 10-12			
Parameter	Range		Median	Range		Median	Units
pH	6.6-	7.2	7	6.5	7.2	7.05	No Units
Acidity	ND-	ND	ND	ND	ND	ND	mg/L
Total Alkalinity	238-	1,630	1,007	215	1,240	725	mg/L
Hardness as CaCO3	3,400-	24,000	4,300	3,500	21,000	5,800	mg/L
Total Suspended Solids	37-	253	95	120	535	242	mg/L
Turbidity	2-	400	9	144	314	239	NTU
Chloride	16,700-	72,400	23,150	9,600	60,800	34,700	mg/L
Total Dissolved Solids	25,000-	98,900	37,800	16,400	97,800	50,550	mg/L
Specific Conductance	53,000	174,000	87,900	34,800	179,000	111,500	umhos/cm
Total Kjeldahl Nitrogen	28-	251	163	26	298	171	mg/L
Ammonia Nitrogen	30-	302	209	18	486	303	mg/L
Nitrate-Nitrite	ND	0.023	0.0115	0.018	0.035	0.0265	mg/L
Nitrite as N	4.5-	96.3	50.4	3.5	38.1	4.7	mg/L
Biochemical Oxygen Demand	93-	323	207	101	2,120	582	mg/L
Chemical Oxygen Demand	2,440-	3,610	2,690	927	3,150	2,945	mg/L
Total Organic Carbon (TOC)	9.5-	26.7	15.5	6.2	36.2	9.75	mg/L
Dissolved Organic Carbon	6.6-	27.8	12.95	5.5	65.3	11.2	mg/L
Oil & Grease (HEM)	110-	110	110	88.2	1430	163.5	mg/L
Cyanide, Total	2.2-	17.9	10.05	6	6	6	mg/L
Amenable Cyanide	ND-	ND	ND	ND	ND	ND	mg/L
Bromide	218-	690	571	117	798	589	mg/L
Fluoride	0-	5.3	2.55	3.5	12.8	3.8	mg/L
Total Sulfide	ND-	0.8	NA	ND	ND	ND	mg/L
Sulfate	145-	1,300	1,055	120	1,260	709	mg/L
Total Phosphorus	0.41-	2.3	0.48	0.19	0.7	0.395	mg/L
Total Recoverable Phenolics	0.0075-	0.0081	0.0078	0.0093	0.23	0.11965	mg/L

Salt concentrations (TDS) in influent water and in flowback water generated over time from the 5 sampling Sites from the Barnett are tabulated in Table 22. As shown in Table 15, influent water contains moderate to low concentrations of salts. Following the use of this water for hydraulic fracturing, a flowback water stream that is collected from the well exhibits increasing concentrations of salts with time. These profiles of salt concentrations are similar to Figure 1. As expected, early flowback water emerging soon after the frac job is relatively low in TDS content; following the initial day, the concentration of total dissolved solids increases with time from low salt concentrations to a plateau of elevated salt levels as measured at 10 and 12 days.

Table 22: Salt Concentrations (TDS, mg/l)

	Day 0	Day 1	Day 3	Day 5	Day 6	Day 7	Day 10	Day 12
LPG 1	203**	31,400	33,500	39,500			48,900	
LPG 2	203**	26,500	37,200	36,100			52,200	
LPG 3	800*	5,850		25,000		30,000		16,400
LPG 4	800*		96,900		98,900		97,800	
LPG 5	800*	23,600						

* One Sample,** One Sample

Levels of total organic carbon (TOC) in the flowback water samples at 5-6 and 10-12 days are lower than the TOC of the raw water. Organic components, as represented by Total Organic Carbon, remain fairly constant or decrease over time (Table 23. The TOC of the Barnett samples is generally lower than that of the Marcellus samples.

Table 23: Total Dissolved Carbon Concentrations (TDS, mg/l)

	Day 0	Day 1	Day 3	Day 5	Day 6	Day 7	Day 10	Day 12
LPG 1	124**	34	17	13			7	
LPG 2	124**	36	15	10			6	
LPG 3	143*	59		27		28		36
LPG 4	143*		19		18		12	
LPG 5	143*	99						

* One Sample,** One Sample

The same observation cannot be made in comparing biochemical oxygen demand (BOD) values in flowback water with the BOD of the influent water streams (Table 24). The BOD data are quite erratic, with sudden spikes to values exceeding 645-2000 mg/l. The moderate levels of BOD in the influent waters may have been due to recycling of recovered water from other frac jobs.

Table 24: BOD (TDS, mg/l)

	Day 0	Day 1	Day 3	Day 5	Day 6	Day 7	Day 10	Day 12
LPG 1	245**	243	290	319			2120	
LPG 2	245**	374	244	323			928	
LPG 3	130*	90		94		645		101
LPG 4	130*		94		92		236	
LPG 5	130*	1480						

* One Sample,** One Sample

COD data (Table 25) shows steady increase with time, roughly following the total salts concentration, indicating that much of the COD may be associated with inorganic matter in the water.

Table 25: COD (TDS, mg/l)

	Day 0	Day 1	Day 3	Day 5	Day 6	Day 7	Day 10	Day 12
LPG 1	559**	1610	1900	2620			2920	
LPG 2	559**	1360	2290	2440			3070	
LPG 3	829*	850		2760		7870		927
LPG 4	829*		5850		360		3150	
LPG 5	829*	4280						

* One Sample,** One Sample

Organic Compounds

As with the Marcellus characterization, organic compounds determined in the characterization of water samples fell into the categories of volatile organics, semi volatile organics, chlorinated pesticides, organophosphorus pesticides, and polychlorinated biphenyls. The following sections summarize the results among all five of the categories of analysis.

Volatile Compounds

As presented in Table 1, samples collected from Sites 1-5 were analyzed for 70 volatile compounds of highly varied chemical characteristics, including the volatile hydrocarbon constituents that are normally found in produced water (such as benzene, toluene, ethylbenzene, and xylenes – or BTEX, and naphthalene) as well as constituents not known to be associated with conventional produced water such as chlorinated solvents and halogenated aromatics. The volatile organic content from the two raw water samples are presented in Table 26. Only traces of napthlene, toluene, and benzene were identified in the sample for Sites LPG 1 and LPG2.

Table 26: Volatile Organics in the Influent Water Samples

Volatiles (µg/L)	LPG 3,4,5	LPG 1,2	Average	Units
Naphthalene	ND	1.3	NA	µg/L
Benzene	ND	2	NA	µg/L
Toluene	ND	3	NA	µg/L

A summary of the results for volatile compound determinations performed recovered flowback water is shown in Table 27. Traces of benzene and other alkylated benzyl isomers were present in the recovered water.   The relative concentrations did not appear to change with time after fracture and appeared to fluctuate fairly randomly. All data were, therefore, consolidated to present the range of results encountered in all 16 samples. It is important to note that of all the components measured in the test protocol, only 8 compounds common to waters generated from petroleum and gas sites were detected. No compound was observed in all 16 samples. The most commonly-encountered constituents were the BTEX and similarly related alkyl-benzene isomers. Traces of acetone, a commonly used cleaning fluid, were also found at measurable concentrations.

Table 27: Summary Volatiles Data; All Site Samples (Days 1-12, Total = 16 Samples)

Volatiles Data (µg/L)	Number of Observations	Range	Median	Average
Isopropylbenzene	2	0.8 - 69	35	35
Acetone	9	27 - 540	110	145
Naphthalene	12	8.3 - 84	22	27
1, 3, 5 - Trimethylbenzene	12	6.4 - 300	15	59
1, 2, 4 - Trimethylbenzene	13	6.9 – 1,200	37	173
Xylenes (total)	14	43 – 1,400	360	425
Benzene	15	49 – 5,300	680	1,198
Ethylbenzene	15	2.2 - 670	29	74
Toluene	15	79 – 8,100	760	1,246

The concentrations of 70 compounds were evaluated in the 16 test samples for a total of 1120 evaluations. Most tests were reported as non-detectable (1013 evaluations). Ninety-two observations were below 1 ppm and only 15 observations were above 1 ppm. Chlorinated, brominated, or other man-made compounds were not detected. More than 90 percent of all constituent determinations, on average, were at

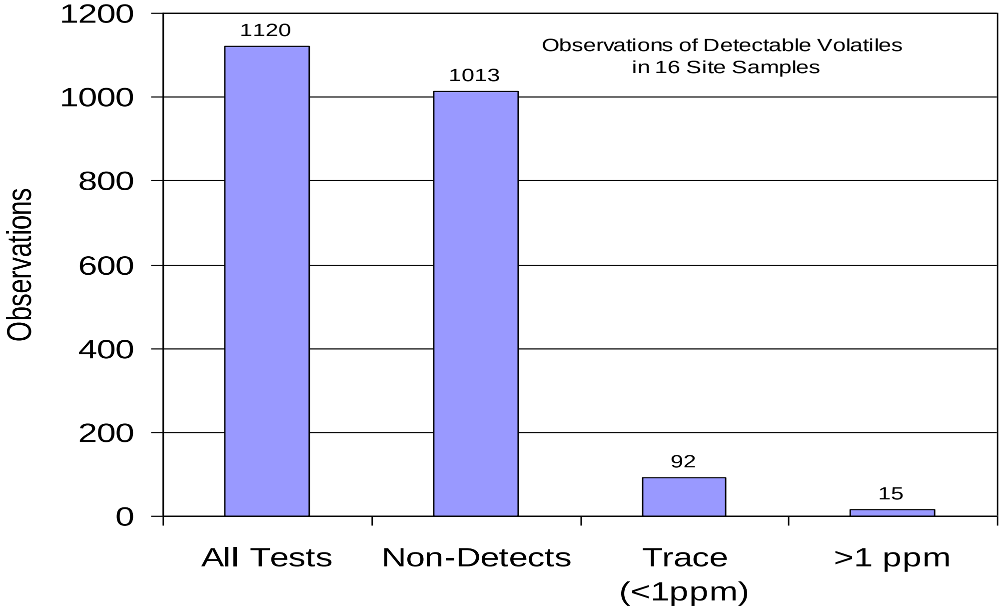


Figure 4: Number of Detectable and Non-Detectable Tests for Volatile Compounds.

non-detectable levels and less than 1.5 percent of all constituent determinations were above 1 ppm (Figure 4 above).

Semi volatile Compounds

A total of 112 semi volatile organic compounds (as listed in Table 1) were included in the analysis of influent water and in flowback water samples. A summary of the results of semi volatile determinations in the two raw water samples is presented in Table 28. The sample from Sites LPG 3,4,and 5 had traces of PAH, and traces of two phthalate esters and two chlorinated hydrocarbons. Water from Site LPG 1 and 2 water had only a single report of pyridine.

Table 28: Semi volatile Compounds in the Influent Water

Semi-Volatiles (µg/l)	LPG 3,4,5	LPG 1,2	Average
Benzo (a) anthracene	1.3	ND	NA
Benzo (a) pyrene	1.1	ND	NA
Benzo (b) fluoranthene	1.3	ND	NA
Benzo (ghi) perylene	1.1	ND	NA
Benzo (k) fluoranthene	0.95	ND	NA
bis (2 - Ethylhexyl) phthalate	36	ND	NA
Butyl benzyl phthalate	2	ND	NA
Chrysene	1.2	ND	NA
Dibenz (a, h) anthracene	0.98	ND	NA
Di - n butyl phthalate	1.9	ND	NA
2, 6 - Dichlorophenol	2	ND	NA
Fluoranthene	1	ND	NA
Hexachlorobenzene	0.8	ND	NA
Indeno (1, 2, 3 - cd) pyrene	0.91	ND	NA
Pentachlorophenol	0.69	ND	NA
Phenanthrene	1.2	ND	NA
Pyrene	1	ND	NA
Pyridine	0.96	40	20.5

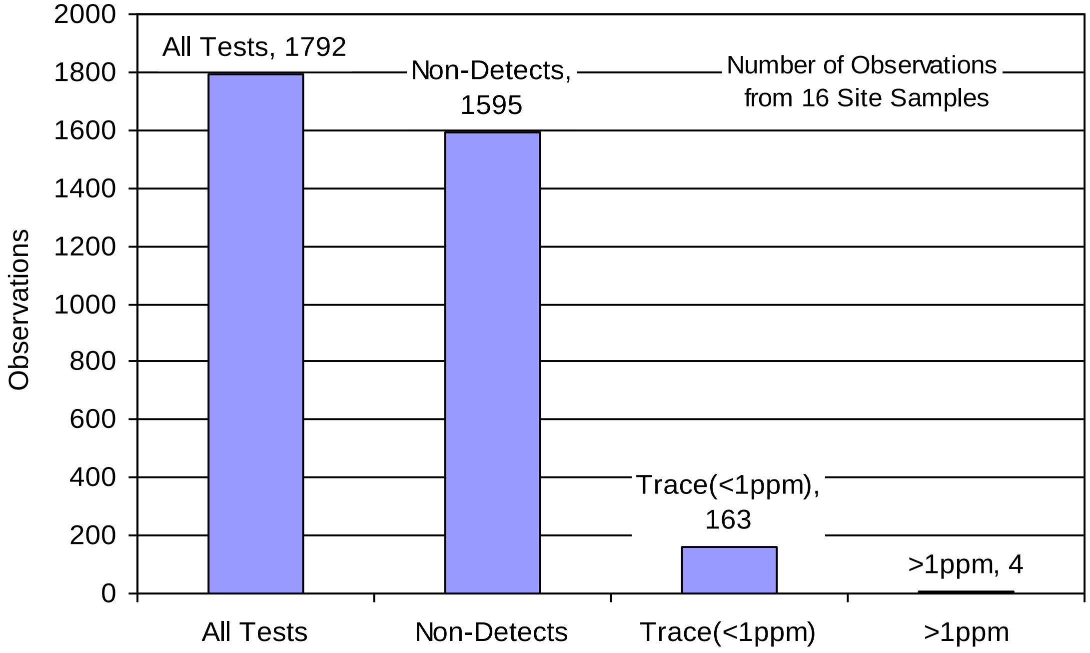


Figure 5: Distribution of Observations of Semi volatile Organics in 16 Site Samples

A summary of the results for semi-volatile compound determinations performed on the 16 site samples is shown in Table 29. Of the 112 compounds in the sample set, about 70% were not detected in any sample. Of the 32 compounds observed, about 1/3 of these were incidental detections in one of the 16 samples. All compounds detected are naturally occurring in petroleum. Pyridine is a nucleophile that is used widely in the manufacture of certain types of chemicals and pharmaceuticals and its presence may be due to its use as a precursor in the manufacture of one of the hydraulic fracturing additives. In general, nearly all of the semi volatile determinations were either non-detect (> 96% of the measurements) or at low trace levels (Figure 5 above).

Table 29:Semi-volatiles Data from 16 Site Samples (Days 1-23) All Five Sites				
Semi-volatiles (µg/l)	Number of Observations	Range	Median	Average
Diphenylamine	2	0.6 - 10.0		5.3
Benzidine	1	ND - 35		
1, 4 - Dioxane	7	3.1 - 12	5.4	6.5
1, 2 - Diphenylhydrazine	2	0.5 - 7.8		4.2
Acetophenone	1	ND - 4.6		
Benzo (a) anthracene	1	ND - 17.0		
Benzo (a) pyrene	1	ND - 130.0		
Benzo (b) fluoranthene	2	0.5 - 84.0		42.2
Benzo (ghi) perylene	2	0.7 - 84.0		42.3
Benzo (k) fluoranthene	2	0.6 - 65.0		32.8
Benzyl alcohol	8	14.0 - 200	27.0	81.5
bis (2 - Ethylhexyl) phthalate	5	4.8 - 490	33	210
Butyl benzyl phthalate	4	1.9 - 110	12.6	34.3
Chrysene	2	0.57 - 240		120
Dibenz (a, h) anthracene	2	3.2 - 150		77
Di - n butyl phthalate	4	1.5 - 120	22	41
2, 4 - Dichlorophenol	1	ND - 15		
2, 4 - Dimethylphenol	8	8.3 - 21	15.5	14.5
Di - n - octyl phthalate	1	ND - 270		
Fluoranthene	1	ND - 0.18		
Fluorene	6	0.46 - 1.3	0.725	0.8
Indeno (1, 2, 3 - cd) pyrene	2	2.9 - 140		71
2 - Methylnaphthalene	16	5.4 - 20,000	22.5	1362
2 - Methylphenol	15	5.8 - 76	31	28.3
3 - Methylphenol & 4 - Methylphenol	15	7.8 - 100	44	41
Naphthalene	16	4.8 - 3100	22	238
N - Nitrosodiphenylamine	2	7.8 - 10		8.9
N - Nitrosomethylethylamine	1	ND - 410		
Phenanthrene	14	0.52 - 1400	1.3	107
Phenol	7	17 - 93	68	63
Pyrene	1	ND - 0.18		0.2
Pyridine	15	100 - 670	500	413

Pesticides

Determinations of the 20 chlorinated pesticides and 3 organophosphorus pesticides on 5 site samples and two source waters (Day 0) are listed in Table 30. A single incidental measurement of less than 0.1 ppb was detected on day 1 from LPG 1. All other determinations for chlorinated pesticides were measured as non-detect. This would suggest that no chlorinated pesticides were introduced with the additives with the influent water during well completions.

Table 30: Summary Pesticide Data

Site	LPG1	LPG2	LPG3		LPG4		LPG5
Sample Day	Day 1	Day 0	Day 0	Day 7	Day 1	Day 5	Day 0
Chlorinated Pesticides							
Chlordane (Technical)	ND	ND	ND	ND	ND	ND	ND
alpha - BHC	ND	ND	ND	ND	ND	ND	ND
beta - BHC	0.073	ND	ND	ND	ND	ND	ND
delta - BHC	ND	ND	ND	ND	ND	ND	ND
gamma - BHC (Lindane)	ND	ND	ND	ND	ND	ND	ND
Heptachlor	ND	ND	ND	ND	ND	ND	ND
Aldrin	ND	ND	ND	ND	ND	ND	ND
Heptachlor epoxide	ND	ND	ND	0.43	ND	ND	ND
Endosulfan I	ND	ND	ND	ND	ND	ND	ND
Dieldrin	ND	ND	ND	ND	ND	ND	ND
4, 4' - DDE	ND	ND	ND	ND	ND	ND	ND
Endrin	ND	ND	ND	ND	ND	ND	ND
Endrin ketone	ND	ND	ND	ND	ND	ND	ND
Endrin aldehyde	ND	ND	ND	ND	ND	ND	ND
Endosulfan II	ND	ND	ND	ND	ND	ND	ND
4, 4' - DDD	ND	ND	ND	ND	ND	ND	ND
Endosulfan sulfate	ND	ND	ND	ND	ND	ND	ND
4, 4' - DDT	ND	ND	ND	ND	ND	ND	ND
Methoxychlor	ND	ND	ND	ND	ND	ND	ND
Toxaphene	ND	ND	ND	ND	ND	ND	ND
Organophospates							
Thionazin	ND	ND	ND	ND	ND	ND	ND
Ethyl parathion	ND	ND	ND	ND	ND	ND	ND
Tetraethyldithiopyrophosphate	ND	ND	ND	ND	ND	ND	ND

Polychlorinated Biphenyls (PCBs)

Determinations of the 7 polychlorinated biphenyl compounds (arochlors) listed in Table 1 were conducted on the two influent waters and Sites 2,4, and 5. As seen from these graphs, all determinations for PCBs were measured as non-detect. This would suggest that no PCBs were introduced with the additives with the influent water during well completions.

Table 31 : PCB Data

	Source Water Day 0		LPG1 Day		LPG2 Day		LPG3 Day	
	LPG 3,4,5	LPG 1,2	1	5	1	5	1	7
Arochlor 1016	ND	ND	ND	ND	ND	ND	ND	ND
Arochlor 1221	ND	ND	ND	ND	ND	ND	ND	ND
Arochlor 1232	ND	ND	ND	ND	ND	ND	ND	ND
Arochlor 1242	ND	ND	ND	ND	ND	ND	ND	ND
Arochlor 1248	ND	ND	ND	ND	ND	ND	ND	ND
Arochlor 1254	ND	ND	ND	ND	ND	ND	ND	ND
Arochlor 1260	ND	ND	ND	ND	ND	ND	ND	ND

Metals

Unlike the organic constituents that do not change much with time, the metals concentrations tend to increase with time from fracture and follow the general trend for TDS. A summary of metal concentrations in the two influent water samples is presented in Table 32.

The total metals content of the Day 1 and Day 3 samples are summarized in Table 34. As seen in this table, sodium is the major cation in all of the samples, followed by concentrations in some samples of calcium, magnesium and barium that will need to be monitored for purposes of scale control in some locations.

The total metal content of the Day 5-6 and Day 10-12 samples are presented in Table 35. Since strontium is present in flowback waters at concentrations between 345 to 4,830 mg/l in the 5-day flowback samples, it will be important for operators to implement procedures to prevent the formation of strontium-bearing scale. Iron levels in the range of 10 to 180 mg/l may also need to be watched and mitigated in order to prevent operational difficulties at a number of well completion locations.

Heavy metals of toxicological concern that are often associated with urban industrial activity (including chromium, copper, nickel, zinc, lead, cadmium, mercury and arsenic) are at very low levels in all of the shale gas water samples.

Table 32: Total Metals in Influent Water Samples

Total Metals	LPG 3,4,5	LPG 1,2	Average	Units
Aluminum	0.525	0.604	0.564	mg/L
Antimony	ND	ND		mg/L
Arsenic	ND	ND		mg/L
Barium	0.0527	2.66	1.356	mg/L
Beryllium	ND	ND		mg/L
Boron	0.509	0.124	0.317	mg/L
Calcium	13.1	17.1	15.1	mg/L
Cadmium	ND	ND		mg/L
Cobalt	ND	ND		mg/L
Chromium	ND	0.0064	0.0064	mg/L
Trivalent Chromium	ND	0.0026	0.0026	mg/L
Copper	ND	ND		mg/L
Iron	1.68	1.18	1.43	mg/L
Lead	0.0127	ND		mg/L
Lithium	0.0464	ND		mg/L
Magnesium	1.57	11.5	6.535	mg/L
Manganese	0.0359	0.0478	0.042	mg/L
Molybdenum	ND	ND		mg/L
Nickel	ND	ND		mg/L
Potassium	3.5	4.46	4	mg/L
Sodium	278	81.3	179.6	mg/L
Selenium	ND	ND		mg/L
Tin	ND	ND		mg/L
Strontium	0.244	1.3	0.77	mg/L
Titanium	ND	ND		mg/L
Thallium	ND	ND		mg/L
Zinc	0.0281	ND		mg/L
Mercury	ND	ND		mg/L

Table 33: Metals Data in the Barnett Samples				
	LPG1,2,3,5 / Day 1		LPG 1,2,4 Day 3	
Metals Data (mg/l)	Range	Median	Range	Median
Aluminum	0.114- 0.572	0.495	0.34- 0.49	0.34
Antimony	ND	ND	ND	ND
Arsenic	ND	ND	ND 0.03	
Barium	0.053 - 3.31	1.50	1.63 - 15.0	2.86
Beryllium	ND	ND	ND	
Boron	0.51 - 39.1	23.5	25.6 - 29.6	29.3
Calcium	13 - 768	564	753 - 6,290	1,270
Cadmium	ND -	0.000	0.00 - 0.00	0.00
Cobalt	0.006 - 0.028	0.014	0.01 - 0.01	0.01
Chromium	0.011 - 0.066	0.030	0.02 - 0.06	0.04
Trivalent Chromium	0.003 - 0.014	0.008	0.02 - 0.02	0.02
Copper	0.087 - 0.131	0.109	0.04 - 0.04	0.04
Iron	ND		18.9 - 43.6	37.4
Lead	0.013 - 0.034	0.013	ND	
Lithium	0.046 - 10.8	9.01	10.7 - 32.3	13.1
Magnesiium	2 - 116	89	113 - 713	199
Manganese	0.036 - 1.98	0.711	0.35 - 1.63	0.66
Molybdenum	0.015 - 0.066	0.043	0.02 - 0.08	0.07
Nickel	0.029 - 0.036	0.033	0.02 - 0.02	0.02
Potassium	4 - 216	111	192 - 662	247
Sodium	278 - 12,200	7805	11,800 - 23,700	14,100
Selenium	ND		0.03 - 0.03	0.03
Tin	0.004 - 0.004	0.004	0.03 - 0.03	0.03
Strontium	ND - 206	132	220 - 1170	282
Titanium	ND		ND	0.00
Thallium	ND		0.05 - 0.05	0.05
Zinc	0.028 - 0.560	0.202	0.14 - 0.18	0.15
Mercury	ND		ND	

Table 34: Total Metals Data Days 5-6 and 10-12

	LPG 1,2,3,4 / Day 5-6		LPG 1,2,3,4 Day 10-12	
	Range	Median	Range	Median
Aluminum	0.37 - 1.64	0.39	0.37 - 2.21	0.43
Antimony	ND	ND	ND	
Arsenic	ND	ND	ND	
Barium	1.48 - 16.8	2.19	0.93 - 17.9	3.6
Beryllium	ND - ND	ND	ND	
Boron	18.0 - 37.1	31.2	7.0 - 31.9	30.3
Calcium	944 - 6,680	1,290	1,110 - 6,730	1,600
Cadmium	ND		ND	
Cobalt	0.01 - 0.01	0.01	0.01 - 0.01	0.01
Chromium	0.01 - 0.11	0.03	0.01 - 0.12	0.03
Trivalent Chromium	0.03 - 0.11	0.07	ND 0.03	0.01
Copper	0.37 - 0.37	0.37	0.06 - 0.52	0.29
Iron	11.8 - 76.7	17.25	12.1 - 93.8	24.9
Lead	ND	ND	0.01 - 0.02	0.02
Lithium	5.10 - 35.6	14.80	2.56 - 37.4	19.0
Magnesiium	145 - 757	182	149 - 755	255
Manganese	0.32 - 1.93	0.42	0.25 - 2.20	0.86
Molybdenum	0.02 - 0.04	0.04	0.02 - 0.03	0.02
Nickel	0.02 - 0.03	0.02	0.03 - 0.05	0.04
Potassium	85 - 725	284	80 - 750	316
Sodium	7,540 - 25,300	15,950	4,370 - 28,200	18,850
Selenium	ND		0.03 - 0.04	0.03
Tin	ND		ND	
Strontium	67 - 1,320	330	48 - 1,550	529
Titanium	0.02 - 0.02	0.02	0.02 - 0.03	0.02
Thallium	ND	ND	ND - 0.14	
Zinc	0.09 - 0.31	0.11	0.10 - 0.36	0.15
Mercury	ND		ND	

DISCUSSION

This report brings to light compositional features of flowback water that are important when considering the possible common and uncommon impacts for this wastewater. Common consideration for treatment considers parameters such as biological oxygen demand, total carbon, total kjdehal nitrogen, oil and greases, etc. It is useful to present a quick summary of these parameters. The following two plots show the median observed common pollutants for the Marcellus samples (Figure 6) and for the Barnett samples (Figure 7).

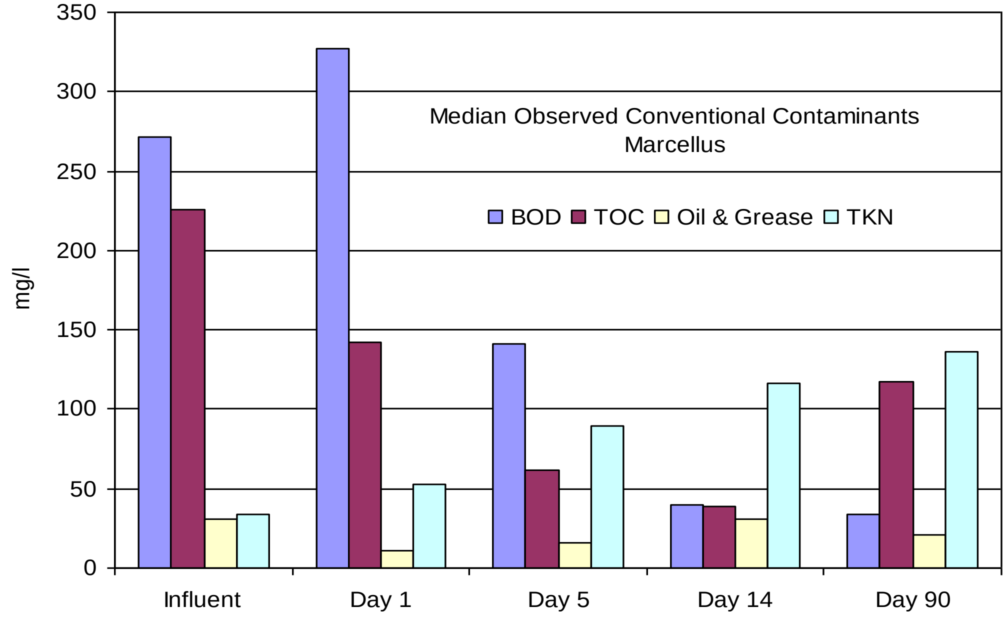


Figure 6: Median Common Components of Flowback Water from the Marcellus Samples

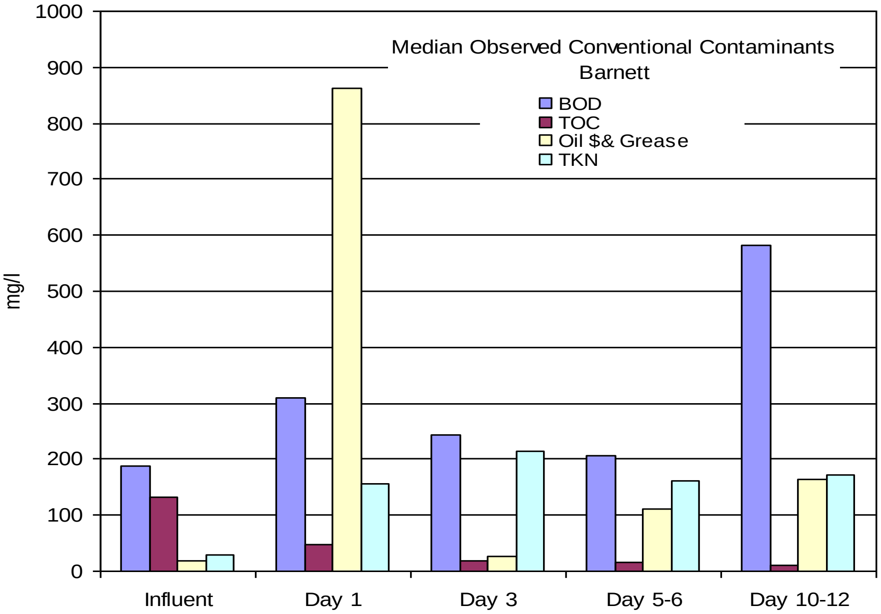


Figure 7: Median Observations of Common Contaminants in the Barnett Samples

Heavy Metals

Heavy metals of toxicological concern that are often associated with urban industrial activity (including chromium, copper, nickel, zinc, lead, cadmium, mercury and arsenic) are at very low levels in all of the shale gas water samples compared to levels reported for municipal wastewaters. Table 35 presents median values from the 5-Day Flowback samples which are compared to median heavy metals concentrations measured in sewage sludges (biosolids) generated by Penn State for the State of Pennsylvania (Steinhouwer, 2000). The comparison shows that the levels of heavy metals of concern are 100 to 10,000 times higher in municipal biosolids (sewage sludges that are routinely transported across communities to disposal sites) than the levels measured in shale gas waters.

Table 35. Comparisons of Median Metals Levels in Shale Gas Waters with Municipal Biosolids (Sewage Sludge)

Metal	5-day Flowback	Sewage Sludge*	Units
Chromium	0.015	35	mg/l
Copper	0.029	511	mg/l
Nickel	< 0.0004	22.6	mg/l
Zinc	0.156	705	mg/l
Lead	< 0.0021	65	mg/l
Cadmium	< 0.0001	2.3	mg/l
Mercury	<0.0002	1.5	mg/l
Arsenic	0.029	3.6	mg/l

* Penn State study reporting median heavy metal content values for Pennsylvania publicly owned treatment works (POTW) biosolids. Stehauwer, et al., 2000.

Total Dissolved Solids, Major Cations and Anions

The tendency for the flow rate of flowback water to decrease, and the total dissolved solids content to increase with time, provides opportunity to capture and reuse early flowback for reuse. The major challenge to the realization of this opportunity is the ultra-high concentration of divalent cations, which have tendencies to cause precipitates and scale in process equipment.

The seven major cations encountered in the flowback waters are sodium, calcium, strontium, potassium, magnesium, iron, barium, and lithium. Of these cations; calcium, barium, strontium, magnesium, and iron are notorious scale formers. The seven major anions measured in these waters are chloride, bicarbonate, bromide, fluoride, sulfide, sulfate, and phosphate. Of these anions, carbonate species, sulfate, and phosphate are known to be potential scale formers.

Figure 8 is a distribution profile of the relative abundance of the major cations in all samples from the Marcellus and the Barnett. Figure 9 is a distribution of the relative abundance of the anions. The calculation for these figures was as follows. Each sample (60 from Marcellus, 19 from Barnett) was treated individually. The value of the each cation species in the individual was compared to the sodium content of the sample, based on the equivalent weight of each cation. The value of the individual anion species was compared to the chloride content. (Note: this presentation considers phosphorous measurements to represent P as phosphate). The equivalent ratio of an ion (example calcium to sodium) from each sample was pooled (60 samples from Marcellus and 19 from the Barnett). The data in the figures represents the median ratio from each pool.

Most of the cation charge is carried by sodium. The proportion of sodium (87% of cation equivalents) in the Barnet samples is somewhat higher than the Marcellus samples (74% of cation equivalents). Chloride is the most common anion, representing more than 93% of the anionic content in the Barnett and 99% in the Marcellus samples. Sodium and Chloride are not shown in Figures 8 and 9 in order to better observe the trends in the less concentrated species.

Calcium is the second most abundant cation, representing about 22% of the cationic charge in the Marcellus and about 9% in the Barnett samples. This difference may, in part be due to the relatively higher content of carbonate alkalinity in the Barnett than in the Marcellus. Calcium also precipitates as a sulfate. The relative sulfate concentration in the Barnett 30 times greater than in the Marcellus. This also suggests a reasonable expectation why the calcium in the Barnett is less abundant than in the Marcellus samples. Calcium is stable at pH< 6. One potential means of handling calcium is by addition of acid to stabilize the calcium. The modest bicarbonate concentration in both sample bases indicates that there is a relatively low buffering capacity. A small acid addition should be sufficient to perform this procedure; therefore, the use of acidification would be very economical for the stabilization (i.e. solubilization) of calcium in the flowback waters of the Barnett and Marcellus Shale Plays.

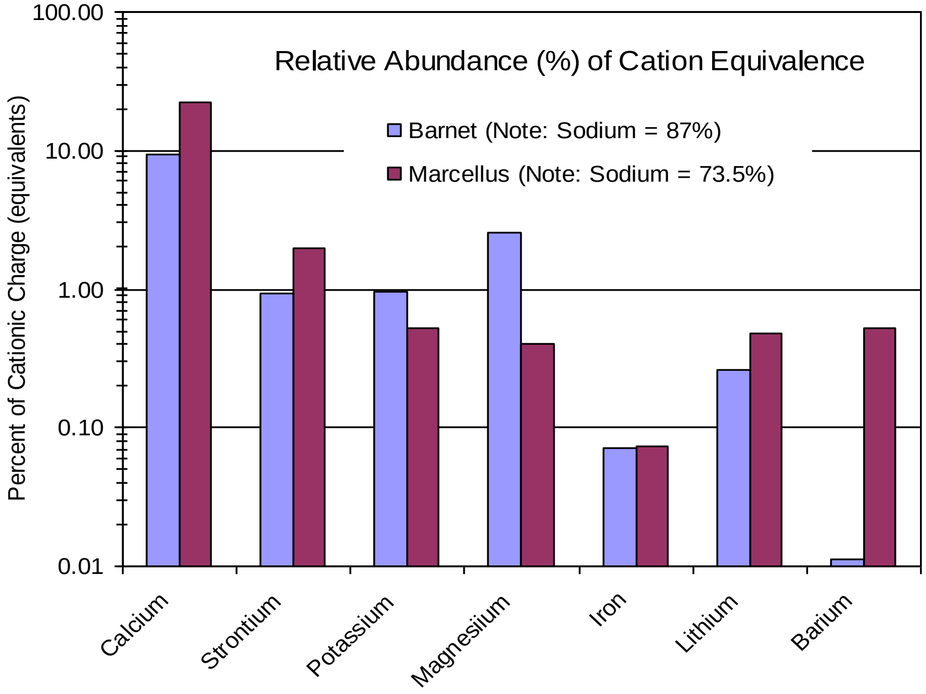


Figure 8: Relative Abundance of Cations in Flowback Waters

Strontium carries 1-2 % of the cationic charge in the flowback waters. Strontium is known to co-precipitate with calcium and barium, either as a carbonate or a phosphate, or a sulfate. Any pretreatment or reuse option should be designed to handle strontium.

Potassium is the fourth most abundant cation, but should not pose any treatment problems. In advanced separation processing, potassium is expected to behave much like sodium.

Magnesium is about as abundant as potassium. Magnesium precipitates at high pH (>11) as a hydroxide, or in phosphate and ammonia rich waters as struvite. These conditions will not likely be found in these waters.

Iron (calculated herein as the ferrous form) will precipitate at pH 5 as a hydroxide. With oxygen present, iron will convert to the ferric form and more readily precipitate at lower pH.   A standard means of controlling iron is aeration followed by caustic addition and settling. Iron is also biologically active, inviting many different types of surface active bacteria that catalyze many redox reactions. These reactions may involve oxygen, carbonate, organic carbon, sulfate, sulfur, and sulfide.

Lithium is present in these waters, but should not interfere with any treatment process. In advanced separation processing, this light metal is expected to behave much like sodium and potassium.

Barium readily precipitates as a sulfate. It is interesting to note that the Barnett water contains much more sulfate than the Marcellus water. This may be one reason why the barium content of the Barnett water has relatively less barium than the Marcellus water.

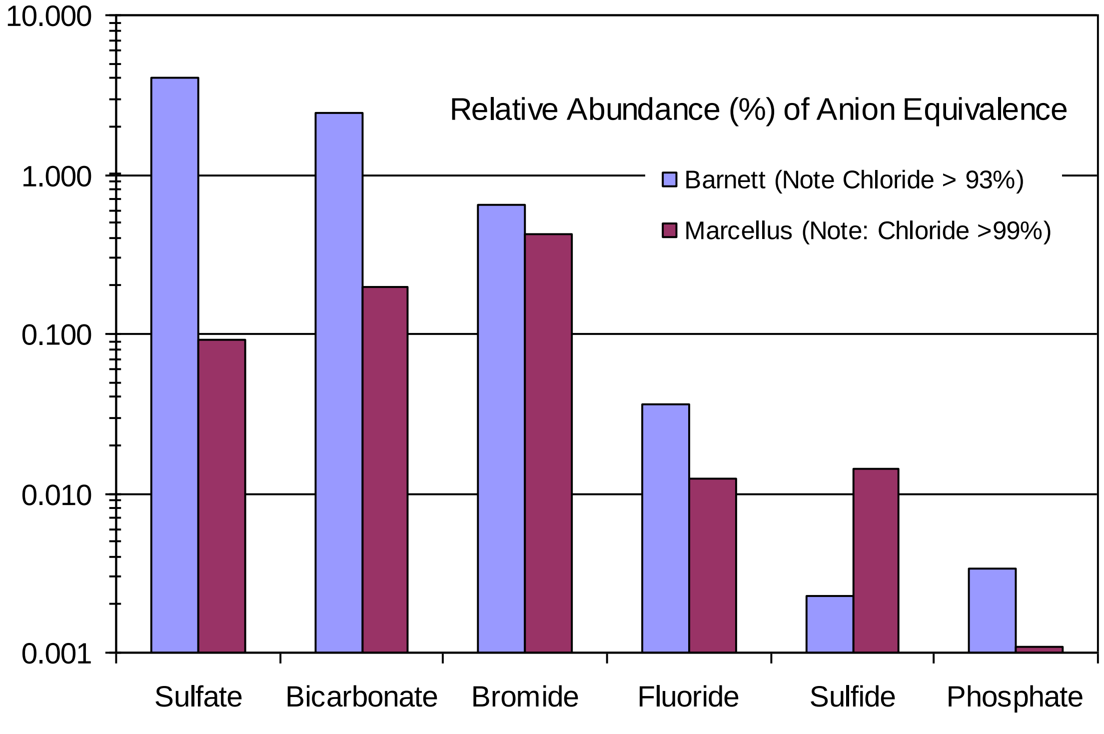


Figure 9: Relative Abundance of Anions in Flowback Waters

Implications for Fate and Transport

As seen in Table 1, the list of measurements and determinations that were pursued in this study were very exhaustive but highly useful in establishing an information base to define a chemical fingerprint associated with flowback waters from these geologic formations. Much of the expense and time required for water characterization has arisen from the extensive effort to analyze the samples for large numbers of volatile and semi volatile organic compounds (including chlorinated pesticides, organophosphorus pesticides and polychlorinated biphenyls); the information base developed in this project strongly suggests that this level of water characterization in the future is not necessary and that monitoring should be focused on measuring constituents that are likely to be present.

A number of observations that are relevant to fingerprinting and to the fate and transport of constituents can be made from consideration of the information base assembled from the first 19 locations in the Marcellus and the first five locations in the Barnett. First, there is clear indication that halogenated hydrocarbon compounds (among volatile, semi volatile, pesticides and PCB categories) and nearly all of the polynuclear aromatic hydrocarbons (of 3 rings and above) are not a part of detectable components in flowback waters. Volatile and semi volatile organic constituents that are normally found in conventional produced waters, such as BTEX, methylated benzenes, naphthalene, naphthenic acids, volatile acids, simple alkanes, etc., are also found in flowback waters and in influent waters for frac jobs that utilize flowback water reuse. However, in terms of fate and transport in the environment, many volatile and semi volatile organics present in shale gas waters are at modest concentrations (most compounds are below 1 ppm). The challenge, therefore, is to choose an alternate parameter that can be used to quickly detect any small release of flowback water that may occur in the course of storage or handling.

A more practical approach might be to use chloride analyses of samples to monitor fate and transport of flowback/produced waters. Chloride has been used as a conservative tracer in hydrogeochemical studies for decades and is well documented in the literature (Clement et al., 2000; Farrell et al., 1994; Lamontagne et al., 2005; Negrel and Lachassagne, 2000; Nelson et al., 2001; Paine, 2003; van Breukelen et al., 1998).

A general overview of the processes controlling the movement of solutes in the subsurface is provided below.

Fate and transport of constituents in the soil/rock/water system is governed by four fundamental processes: advection, dispersion, retardation, and decay. Advection is simply the mass movement of a solute along with groundwater and is modeled by Darcy's Law. Dispersion is a mathematical description of diffusion and mechanical mixing of a solute in a system. Diffusion is modeled using Fick's first and second law. Dispersion is an empirical correction factor controlled by the physical properties of the soil/rock matrix (porosity, grain size, sorting, etc) and scale of the system. Retardation is the process by which non conservative solutes interact with the soil/rock and their movement downgradient is subsequently slowed. It is modeled by a linear equation that is a function of porosity, moisture content, bulk density, and the humic organic matter content. Examples of retardation reactions are adsorption-desorption, ion exchange, precipitation-dissolution, and oxidation-reduction reactions. Decay is the process by which a solute is removed from the system due to chemical reactions, biological reactions, and/or radioactive decay and is modeled using the appropriate equation for the reaction occurring in the system.

Conservative solutes are ones that can be modeled using only advection and dispersion. Common examples are chloride and bromide, but bromide levels in the samples collected as part of this study were several orders of magnitude lower than chloride levels. Non-conservative solutes can only be modeled using advection, dispersion, retardation, and/or decay. Examples of non-conservative solutes are volatile/semi volatile organics (e.g. benzene, toluene, PAHs, PCBs, etc.), sulfate, iron, and many others. Non-conservative species subsequently migrate slower throughout the subsurface than do conservative tracers and therefore are inappropriate to use as indicators of Marcellus Shale flowback water impact to a system. Nearly all classes of volatile and semi volatile organics discussed in this report have been shown to be sequestered to various types of soils, thereby significantly retarding their mobility in the environment (Linz and Nakles, 1997).

Chloride, on the other hand, is more mobile and has considerable potential as an early sentinel indicator of flowback water impacts due to a number of advantages. In addition to being conservative (by virtue of its non-volatile, non-sequestering, non-reactive property), chloride is usually present in relatively high concentrations ranging from 10,000 to 200,000 mg/l, ten to a hundred times the concentration of most inorganics and more than a million times the levels of most volatile and semi volatile organic constituents. Chloride is also easily measured with field kits that can determine the presence of this anion with small samples, and verified in its presence with simple conductivity instruments. Due to its high concentration and its ubiquitous presence in flowback waters, chloride anion is an excellent monitoring tool for even the smallest leaks of flowback water into the environment.

CONCLUSIONS

With the completion of this sampling and analysis effort, the following conclusions can be drawn from the results:

1. General chemistry characterization of flowback water indicates that values for pH, alkalinity, total dissolved solids, total organic carbon, oils and greases and other parameters from general water characterization are well within the normal ranges reported for conventional produced waters. Flowback water appears similar in composition to conventional produced water, even in the presence of additives employed for performing hydraulic fracturing.
2. Shale gas flowback water cations are dominated by sodium and calcium; anions are dominated by chloride.
3. Metals in flowback water are well within the ranges for normal produced waters. Industrial heavy metals (e.g. chromium, copper, nickel, zinc, lead, cadmium, arsenic and mercury) are a small fraction (less than 1 percent) of the heavy metals content found in municipal biosolids generated from POTW's.
4. Among volatile organic compounds, more than 93% of these constituents were found at non-detectable levels and less than 1% were above 1 ppm for any of the 5 sampling events among 19 locations. The data indicate that the constituents above 1 ppm are those that are a normal part of produced waters associated with natural gas operations (such as xylenes, toluene and naphthalene).
5. Among semi volatile organic constituents, more than 96% of all determinations were at nondetectable levels and less than 0.1% of these constituents were above 1 ppm.
6. All chlorinated pesticides, organophosphorus pesticides and polychlorinated biphenyls were determined to be at non-detect levels for all tested samples of influent water and flowback waters.
7. Virtually, all man-made halogenated organic compounds were at non-detect levels; the same was true for organophosphorus pesticides. This strongly suggests that additives that are blended with influent waters do not contain concentrations of man-made organic chemicals of concern.

8. The results of this shale gas water characterization effort indicate that pesticides, PCBs, a large fraction of the volatile and semi volatile constituents should be considered to be unnecessary for the sampling and analysis of flowback waters in the future.
9. Determination of factors that affect levels of organic and inorganic compounds could potentially be determined through a correlation of flowback water composition with the key shale gas development parameters of geographic area, depth of wells, completion methods, etc.

REFERENCES CITED

APHA. 1992. "Standard Methods for the Examination of Water and Wastewater", 18th Edition (SM18).

APHA. 1999. "Standard Methods for the Examination of Water and Wastewater", 20th Edition (SM20).

Clark, C.E. and J.A. Veil. 2009. Produced Water Volumes and Management Practices in the U.S. USDOE/Argonne Laboratories Report No. ANL/EVS/R-09/1.

Clement, T.P., Johnson, C.D., Sun, Y., Klecka, G.M., and Bartlett, C., 2000, Natural attenuation of chlorinated ethene compounds; model development and field-scale application at the Dover site: Journal of Contaminant Hydrology, v. 42, p. 113-140.

Engelder, T., and G.G. Lash. 2008. Marcellus Shale Play's Vast Resource Potential Creating a Stir in Appalachia. The American Oil & Gas Reporter, May.

Farrell, D.A., Woodbury, A.D., and Sudicky, E.A., 1994, The 1978 Borden tracer experiment; analysis of the spatial moments: Water Resources Research, v. 30, p. 3213-3223.

Gaudlip, A.W., L.O. Paugh, and T.D. Hayes. 2008. Marcellus Shale Water Management Challenges in Pennsylvania. SPE Paper No. SPE–119898-PP, Society of Petroleum Engineers.

Hayes, T.D. 2009. Sampling and Analysis of Water Streams Associated with the Development of Marcellus Shale Gas, Final Report to the Marcellus Shale Coalition. Gas Technology Institute, Des Plaines, Il.

Kharaka, Y.K. and C.A. Rice. 2004. "Organic and Inorganic Species in Produced Water: Implications for Water Reuse", Proceedings of the Natural Gas Technologies Conference, Phoenix, Feb 8-10. Available from the Gas Technology Institute

Lamontagne, S., Leaney, F.W., and Herczeg, A.L., 2005, Groundwater-surface water interactions in a large semi-arid floodplain; implications for salinity management: Hydrological Processes, v. 19, p. 3063-3080.

Linz, D.G. and D.V. Nakles. 1997. Environmentally Acceptable Endpoints in Soil. American Academy of Environmental Engineers, United Book Press, Inc., Baltimore, MD.

Negrel, P., and Lachassagne, P., 2000, Geochemistry of the Maroni River (French Guiana) during the low water stage; implications for water-rock interaction and groundwater characteristics: Journal of Hydrology, v. 237, p. 212-233.

Nelson, M.D., Parker, B.L., Al, T.A., Cherry, J.A., and Loomer, D., 2001, Geochemical reactions resulting from in situ oxidation of PCE-DNAPL by KMnO (sub 4) in a sandy aquifer: Environmental Science & Technology, v. 35, p. 1266-1275.

Paine, J., 2003, Determining salinization extent, identifying salinity sources, and estimating chloride mass using surface, borehole, and airborne electromagnetic induction methods: Water Resources Research, v. 39, p. 10.

Stehouwer, R.C., A.M. Wolf, and W.T. Doty. 2000. “Chemical Monitoring of Sewage Sludge in Pennsylvania: Variability and Application Uncertainty.” J. Environ. Qual. 29: 1686 – 1695.

USEPA. 1984. “Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater”, 40CFR, Part 136, Appendix A, October 26.

USEPA. 1983. “Methods for Chemical Analysis of Water and Wastes”, EPA-600/4-79-020, March.

USEPA. 1986. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods”, Third Edition, November (SW846).

USGS. 2009. USGS Produced Water Database. Available at: http://energy.cr.usgs.gov/prov/prodwat/intro.htm .

van Breukelen, B.M., Appelo, C.A.J., and Olsthoorn, T.N., 1998, Hydrogeochemical transport modelling of 24 years of Rhine water infiltration in the dunes of the Amsterdam water supply: Journal of Hydrology, v. 209, p. 281-296.

ACKNOWLEDGEMENTS

The data presented in this report from the Marcellus Shale was generated from a project conducted in 2009 under the funding of the Marcellus Shale Coalition. A summary of the report is available from Gas Technology Institute upon request (Hayes, 2009).

APPENDIX A: FIELD SAMPLING AND ANALYSIS PLAN (FSAP)

Appendix A

Field Sampling and Analysis Plan (FSAP)

FIELD SAMPLING AND ANALYSIS PLAN

DEVONIAN SHALE FLOW BACK WATER CHARACTERIZATION STUDY

Prepared by

Appalachian Shale Water Conservation and Management Committee

December 2008

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1.0 INTRODUCTION

This Field Sampling and Analysis Plan (SAP) details the procedures for sampling and field documentation to be utilized for the characterization study of the fracturing and flow back fluids associated with the Devonian shale. The FSAP has been prepared to ensure that all data and information gathered are properly sampled, documented, and technically sound. The FSAP and Quality Assurance Project Plan (QAPP) together comprise the Sampling and Analysis Plan (SAP).

1.1 PURPOSE

The FSAP includes a detailed description of field sampling procedures to be conducted. The procedures described are consistent with the RCRA Technical Enforcement Guidance Document (TEGD), U.S. EPA, 1989; RCRA Facility Investigation Guidance Document (U.S. EPA, May 1989); RCRA Ground Water Monitoring; Draft technical Guidance (U.S. EPA, 1992); Data Quality Objectives for Remedial Response Activities (U.S. EPA, 1987).

The SAP consists of 5 sections. Section 1.0 includes a brief description of the data objectives and a brief discussion of the project. 2.0 provides information regarding documentation, quality assurance/quality control (QA/QC) requirements, and reporting. Section 3.0 addresses the sampling procedures. Section 4.0 describes the proper handling requirements of any investigative derived waste generated. Reference documents are provided in Section 5.0

1.2 DATA OBJECTIVES

The data objectives will address characterization of the fracturing and flow back fluids associated with the development of the Devonian shale. This characterization study will:

- Identify the specific constituents of interest (COI) associated with flow back water;
- Reduce/eliminate the allegations that the chemicals used for fracturing will contaminate groundwater; and
- Provide sufficient information for the selection of proper disposal techniques.

Achieving these data objectives will require obtaining data of acceptable levels of certainty. Therefore, it is essential that the field and sampling procedures be completed under stringent and appropriate methods.

1.3 BACKGROUND

The process of developing Devonian Shale wells requires increasing the number of fractures and extending the existing fractures. Fracturing is necessary to obtain a greater volume of natural gas from the Devonian Shale at in a cost-efficient manner. Fracturing uses high volumes and high-pressure chemically treated water or a gel to induce fractures in the shale surrounding the well bore. Most applications require between 500 and 10,000 psi.

Fracturing is done by isolating off a portion of the well and injecting chemically treated water or gel and sand with cement, perforating, under very high pressure into the isolated portion of the well bore. Generally, 1.5 to 5 million gallons of water is pumped into the formation of a vertical or horizontal well, respectively. The high pressure fractures the shale and sand keeps the fractures open. A drop in pressure indicates that the formation has accepted water.

To prevent the fractures from closing when the pressure is reduced several hundred tons of sand or other propant is pumped down the well and into the pressurized portion of the well. When the fracturing occurs the sand is forced into the fractures. If enough sand is trapped in the fractures it will prop the fractures open when the pressure is reduced. The propped fractures provide an increase in the permeability for gas flow.

Approximately 25 to 30 percent of the water used in fracturing is recovered. This flow back water is currently a concern because there is a limited amount data. The ASMCWC is conducting this study in an effort to characterize the flow back water associated with the Devonian Shale.

The flow back water will be collected in either an on-site off-stream temporary impoundment or a series of frac tanks.

2.0 CHARACTERIZATION STUDY OF FLOW BACK WATER

Fracturing is completed over several days depending on the geological formation. Because the flow back water is under pressure, initially the flowback water is recovered at a faster rate in the beginning of fracturing and significantly declines as facturing continues and the well is released to production. The initial concentrations at the start of fracturing (high yields of flow back water) should yield lower concentrations of constituents of interest (COI). It is assumed that the concentration of the fracturing chemicals remain constant throughout the flow back regardless of the rate of return. However, the increase concentration of in the COI is due to a longer residence time in the applicable formation and not associated to the additives of the fracing fluids. Therefore, to obtain representative samples of the flow back water samples will be collected on three separate days (i.e., days 1, 5 and 14). The data obtained from day 14 should represent the chemical characteristics of the natural formation fluid.

Additionally, a baseline sample of the fracturing fluid will be collected prior to injection. The baseline sample will contain the materials (e.g., water and chemicals) used in the fracturing process. A sample will also be collected from a well in Devonian shale that has been in production for a period of time (i.e., a well that has been in production for more than 3 months). The data obtained from this well should represent the chemical characteristics of the natural formation fluid. The analytical results associated with these samples will assist in the data interpretation.

2.1 Sampling and Analyses

In general, several frac tanks are connected in-line and filled simultaneously with the flow back water. This is completed to avoid back pressure when shutting one frac tank and opening another tank for additional capacity. This filling process will provide a composite sample of the flow back water over time. To minimize volatilization, a representative composite sample of the flow back water samples will be collected from the top of a frac tank or flow back impoundment.

The flow back water is either pumped into the frac tanks for storage until the water is disposed of properly. If a project does have an impoundment that stores flow back water on site in an impoundment, a grab sample will be collected from the impoundment following day 1, 5 and 14 of fracturing.

The base fracturing fluid will be collected prior to going down hole. The base fracturing fluid will be collected from either the sampling lines built into the blenders or as a grab sample from the blending containers. In either case a representative sample of the fluid will be collected.

Numerous flow back water samples will be collected from several unique locations. Phase one of this characterization study will include the sampling of six flow back water samples from six unique locations.

The list of constituents recommended for the characterization study was developed from comments received from the Pennsylvania Department of Environmental Protection (PADEP), the West Virginia Department of Environmental Protection (WVDEP) and members of the ASWCMC. Because the recommended list of constituents is extremely extensive, it was decided that one sample from each site will be completed for the full list of recommended constituents (Table 1). All other samples will be sampled for a subset of these constituents (Table 2), which are based on generator knowledge and Group 1 and Group 2. The analytical results of phase one of the characterization study will determine the list of constituents of subsequent sampling events.

3.0 SAMPLING PROTOCOLS

This section identifies the protocols to be implemented during field sampling. Specifically this section describes the preparation, documentation, and reporting procedures to be used that will assure quality assurance and quality control.

3.1 PROJECT INITIATION

Following acceptance of this plan by the ASWCMC and the state agencies, Gas Technology Institute (GTI) will authorize Test America an independent a credited analytical laboratory to provide the appropriate sample containers and preservatives; and URS, an independent environmental consulting company has been retained to collect the flow back water. Furthermore, Test America will complete the analytical analyses. Test America is certified by WVDEP and PADEP.

The regulatory agencies are invited to collect split samples. The samples will be collected at the discretion of the agency. All agency sampling must be approved and coordinated with the appropriate gas company.

3.2 DOCUMENTATION

A field logbook and chain-of-custody form will be utilized during the field activities.

3.2.1 Field Logbook

During field activities, a site-specific logbook will be used for documentation of all notes. It is recommended that each page of the logbook be numbered and dated. The entries should be legible and contain accurate and inclusive documentation of the project activities. Once completed, the logbook becomes an accountable document and is maintained as part of the project file. The logbook should include, at a minimum, the following information:

- Identification of logbook ownership and telephone number on the inside front cover;
- Well location and identifying number;
- Names of field personnel at the site;
- Weather information (general);
- Sample locations and activities;
- Sample collection equipment;
- Date and time of monitoring of sampling;
- Water quality measurements (field pH, specific conductance, water temperature);
- Field instrument calibration information;
- Visual observations;
- Collection of field quality assurance samples (i.e., blanks or duplicates);
- Regulatory agency personnel observing sampling;

- Enter agency, collector's name, samples splits, etc., if a regulatory agency splits samples; and
- Documentation of sample shipment dates, time, and carrier tracking (air bill) number, if necessary.

Copies of the field book pages will become part of the sample data package.

3.2.2 Chain-of-Custody Form

The chain-of-custody form is used to record the custody of all samples collected. This chain-of-custody form documents transfer of the custody from the sampling personnel to another person, to the laboratory, or to another party, such as a courier delivery service. The chain-of-custody form also serves as a sample logging mechanism for the laboratory sample custodian.

When the field personnel sends samples to the analytical laboratory, each cooler chest containing samples must be accompanied by a chain-of-custody form. These forms contain the following information pertaining to the samples:

- Project Name
- Name(s) and signature(s) of the individual(s) collection the samples;
- Sample location;
- Date and time of sample collection;
- Total number of sample containers per sample location;
- Type of sample preservation used (e.g., HNO_3, HCl, etc.)
- Analytical parameters of interest for each sample and number of containers per analytical parameter;
- Remarks or observations;
- Signature(s) of all individual(s) relinquishing and receiving custody of the samples;
- Name of the carrier shipping the samples; and
- Air bill number under which sample containers(s) was sent, if applicable;

The chain-of-custody forms are multi-colored carbon copy forms. The original copy (white) is submitted to the laboratory with the samples, the second copy (pink) is sent to GTI, and the third (yellow) is kept for the project files.

3.3 SAMPLE DESIGNATION AND IDENTIFICATION

Each sample collected for this characterization study will be assigned a unique sample tracking number. The identification of the well location and participating gas company will not be identified. All well locations will be blind. GTI will assign each well a project identifier. The project identifier will be a unique single alphanumeric letter that will identify the Devonian Shale well location and company. This unique alphanumeric letter will be provided to the third party environmental consultants to be used in the sample designation.

3.4 SAMPLE MANAGEMENT AND SHIPMENT

The possession of samples or other physical evidence shall be traceable from the time the samples are obtained until they have been submitted to the analytical laboratory. To simplify the documentation of possession that is maintained on the chain-of-custody form, the number of people who handle the sample during the investigation should be minimized. All samples will be documented in the field logbook, on the chain-of-custody form and on the sample container labels. Field documentation procedures are provided above in Section 2.3 and the in the QAPP.

Sample labels shall be completed for each sample using waterproof non-erasable ink. All samples are to be sealed immediately upon collection and are to be immediately place on ice in a cooler.

Samples are to be properly packaged for shipment and delivery to the laboratory. To ensure that the samples are kept cold for preservation requirements, the samples are to be shipped in iced coolers for overnight delivery. Samples collected during the characterization study are to be classified as environmental samples.

Shipping containers are to be secured with tape and use of security seal method to ensure that the cooler may not be opened without evidence of the seal being tampered.

Ice used to keep the samples cooled must be secured in plastic bags (e.g., Zip-Lock® plastic bags) to ensure that melted ice does not cross contaminate the samples pr leak from the coolers.

Samples will be either hand delivered to the laboratory or shipped via priority service to the laboratory or the air bill retained for the project file.

4.0 SAMPLING EQUIPMENT AND PROCEDURES

Grab samples will be conducted using a new PVC bailer from the top of the frac tank. The order, in which the grab samples are collected, as prioritized to the sensitivity to volatilization, is as follows:

- Volatile Organics
- Purgeable Organics
- Purgeable Organic Halogens
- Total Organic Halogens
- Total Organic Carbon
- Extractable Organics
- Total Metals
- Dissolved Metals
- Phenols
- Cyanide
- Sulfate and Chloride
- Turbidity
- Nitrate and Ammonia

There is not an order of preference for the collection of the remaining conventional parameters.

Temperature, pH, dissolve oxygen, and specific conductance measurements will be completed in the field

5.0 INVESTIGATION DERIVED WASTE

Materials which may be investigation derived waste (IDW) are:

- Personnel protective equipment (PPE), including disposable gloves, coveralls, booties, etc.;
- Disposable equipment, including plastic ground and equipment covers, aluminum foil, Composite liquid waste samplers (COLIWASAs), used sample containers, tape, etc.;

5.1 MANAGEMENT OF HAZARDOUS IDW

If wastes are suspected to be hazardous, appropriate analysis must be performed to make that determination. The analytical testing should meet the requirements of the potential disposal characterization requirements. If the IDW is determined to be hazardous wastes either through testing of characteristics or as a listed waste, they must be properly container and labeled. They may be stored on site for a maximum of 90 days before they must be manifested and shipped to a permitted treatment of disposal facility.

Care should be taken to keep non-hazardous materials segregated from hazardous waste-contaminated materials.

6.0 REFERENCES

Kitrell, F.W. 1990. A Practical Guide to Water Quality Studies.

U.S. EPA, 1986. Test Methods for Evaluating Solid Waste, Volume II; Field Manual, Physical/Chemical Methods. Office of Solid Waste and Emergency Response, SW-846, November 1986

U.S. EPA 1987. Data Quality Objectives for Remedial response Activities. Oswer Directive 935507B, Office of Emergency and Remedial Response, Washington DC. EPA/5406/6=87/100 and 004.

U.S. EPA, 1986. RCRA Ground-Water Technical Enforcement Guidance Document. Office of Waste Programs Enforcement, Washington DC, Oswer Directive 99501.

U.S. EPA, 1992. RCRA Groundwater Monitoring: Draft Technical Guidance. Office of Solid Waste, Washington DC. EPA/530/R-93/001.

U.S. EPA, 1998. Environmental Investigations Standard Operating Procedures and Quality Assurance Manual. U.S. EPA Region 4, Athens, GA, May 1996.

APPENDIX B: QUALITY ASSURANCE PROJECT PLAN (QAPP)

Appendix B

Quality Assurance Project Plan (QAPP)

QUALITY ASSURANCE PROJECT PLAN

DEVONIAN SHALE FLOWBACK WATER CHARACTERIZATION STUDY

Prepared by

Appalachian Shale Water Conservation and Management Committee

November 2008

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TABLES

1.0 PURPOSE

This document is the Quality Assurance Project Plan (QAPP), which provides specific quality assurance/quality control (QA/QC) procedures to be executed and supported for the Characterization Study of the flow back water associated with the well fracturing of the Devonian Shale.

Data generated for environmental purposes must be technically sound and legally defensible, and supported by defined and verified limits of confidence. Therefore, the objective of this QAPP is to ensure the generation of accurate, precise, representative and complete data. The QAPP sets forth the data collection procedures and data evaluation processes, which will ensure that appropriate levels of data quality are obtained.

Analyses must meet the QA/QC requirements associated with this QAPP and the following documents:

SW-846, Third Edition (September 1986), as amended by updates 1 (July 1992), II (September 1994), IIA (August 1993), and IIB (January 1995), or the most current SW-846 update;

EPA's "Handbook for Analytical Quality Control in Water and Wastewater Laboratories" (EPA 600/1-79-019);

Standard Methods for the Examination of Water and Wastewater.

Only U.S. EPA-approved methods will be used for chemical analyses. Any omission in this QAPP of relevant requirements, tasks and other items found in the referenced methods does not constitute a waiver of the omitted requirement, task, or item. It is the responsibility of all personnel involved in the various site investigation activities to perform and document the required procedures designated herein.

2.0 PROJECT DESCRIPTION

The Appalachian Shale Water Conservation and Management Committee (ASWCMC) is conducting a study to characterize the fracturing and flow back water generated from development of Devonian Shale wells.

2.1 SCOPE OF WORK

Samples will be collected from both vertical and horizontal Devonian Shall gas wells. Numerous samples will be collected from several locations. Phase one of the characterization study will include 4 grab samples from 6 well sites. A sample will also be collected from a well that has been in production for at least three months. The following grab samples will be collected from each site:

- One baseline fracturing water sample that includes the fracturing chemicals, excluding the sand;
- Flowback water samples will be collected on days 1, 5 and 14 of the following the fracturing process; and
- Water from an existing producing well.

The list of constituents recommended for the characterization study was developed from comments received from the Pennsylvania Department of Environmental Protection (PADEP), the West Virginia Department of Environmental Protection (WVDEP) and members of the ASWCMC. Because the recommended list of constituents is extremely extensive, it was decided that one sample from each site will be completed for the full list of recommended constituents (Table 2). All other samples will be sampled for a subset of these constituents (Table 3), which are based on generator knowledge. The analytical results of phase one of the characterization study will determine the list of constituents of subsequent sampling events.

In addition, field measurements of pH, specific conductance, temperature, dissolved oxygen, and turbidity will be taken of flow back aqueous samples.

3.0 QUALITY ASSURANCE OBJECTIVES FOR MEASUREMENT DATA

Data Quality Objectives (DQOs) are qualitative and quantitative statements to ensure that data of known and appropriate quality are obtained during the characterization study (sampling and analysis).

The data objectives will address characterization of the flow back fluids associated with well fracturing generated from Devonian shale. This characterization study will:

- Identify the specific constituents of interest (COI) associated with flow back water;
- Reduce/eliminate the allegations that the chemicals used for fracturing will contaminate groundwater; and
- Provide sufficient information for the selection of proper disposal techniques.

- Achieving these data objectives will require obtaining data of acceptable levels of certainty. Therefore, it is essential that the field and sampling procedures be completed under stringent and appropriate methods

3.1 DATA QUALITY LEVELS

There are typically five analytical levels of data quality available to accomplish the objectives of investigations of this type. These levels are typically designated as follows:

Level I: field screening or analysis using portable instruments, calibrated to non-compound specific standards;

Level II: field analysis using portable instruments, calibrated to specific compounds;

Level III: non-Contract Laboratory Program (non-CLP) laboratory methods;

Level IV: CLP Routine Analytical Services (RAS) methods; and

Level V: non-standard analytical methods.

DQO Levels I and III will be used to characterize the Devonian Shale Fracturing Flowback sampling activities. The following sections describe the use of the analytical procedural levels that will be used during the project.

Field Screening Methods - Level I

Field determinations of pH, specific conductance, temperature, dissolved oxygen, and turbidity will be made during characteristic sampling as part of a field screening procedure. These analytical methods are used to determine stability of the well and they are typically designated as Level I data quality.

In addition, as part of the health and safety program, worker safety may be monitored via one or more of a variety of field screening tests such as a photoionization detector (PID) or flame ionization detector (FID) to test for volatile organic vapors, or a combustible gas indicator to test for explosivity potential. These tests, which are semi-quantitative, are classified as field screening evaluations, even though they typically are not used for site characterization purposes.

Non-CLP Laboratory Methods - Level III

Level III analytical procedures provide precise, accurate and defensible data for the intended data uses, with a less formal documentation and reporting nomenclature at reduced analytical costs over Level IV data quality procedures. Data Quality Level III will be used during this characterization study. Table 1, summarizes analyses that will be conducted to characterize and quantify constituent concentrations.

3.2 QUALITY CONTROL PARAMETERS

The exact quantitative criteria used to evaluate data quality from the laboratory's precision and accuracy perspective for the aqueous and solid sampling media will be presented in the selected laboratory Quality Assurance Manual(s) (Appendix QAPP-1 and following). The following is a description of terms that appear in the QAM.

Reference: The reference of the U.S. EPA standard analytical methodology used for each procedure.

Precision: A measure of the mutual agreement among individual measurements of the same property under prescribed similar conditions. Precision is evaluated based on the relative percent difference (RPD) between duplicate matrix spike results or duplicate sample results, as appropriate. The matrix spike duplicate RPD limits are parameter and method-specific, MS/MSD RPD QC limits will be presented in the laboratory QAMs. Laboratory duplicate sample RPD limits are typically 20 percent for aqueous media and 35 percent for solid media (exceptions may apply for solid media whose samples may be nonhomogeneous). Field duplicates are also evaluated by calculating the RPDs between field duplicate sample results. However, evaluations of field duplicate RPDs are used as advisory determinations since numerous factors in sampling and analysis may cause variances between field duplicate results.

Accuracy: The degree of agreement of a measurement with an accepted reference or true value. Accuracy is evaluated based on the percent recovery of spiked samples. The matrix spike recoveries for organic analyses are method and parameter specific and are typically used as an advisory QA/QC measure due to the difficulty associated with recovering spiked organic parameters. Organic parameter percent recovery QC limits will be presented in the laboratory's QAM. The matrix spike recoveries for inorganic and most conventional parameters are typically a range of ±25 percent.

Completeness: A measure of the amount of valid data obtained from a measurement system compared to the amount expected to be obtained under normal conditions. The method of calculation for percent completeness is defined in Section 12.3. Completeness can be evaluated in two ways: 1) by comparing the number of samples actually collected to the expected number of samples to be collected; and 2) by comparing the number of valid analyses received from the laboratory to the number of actual samples collected. The results of any Level III analyses to be performed is typically used for characterization studies and as such will have a minimum completeness of 95 percent for both evaluations of completeness.

Exact QA/QC criteria the laboratory will use to evaluate its data's precision and accuracy will be provided following selection of the analytical laboratory, if the criteria are not method-specific.

Table 1 summarizes the individual parameters and associated reporting limits.

There are also qualitative criteria that are adhered to ensure that data of known and appropriate quality are obtained during investigation activities. These criteria include representativeness and comparability.

The sampling and analysis programs are designed to ensure that analytical data obtained during the characterization study represent current conditions found at the site and produce data of comparable quality. The sampling frequency was selected to ensure data are suitable for their intended use and adequately characterize the flow back water. Additionally, standard recognized analytical methodologies will be utilized to ensure comparability. These designs are instituted to ensure appropriate sample representativeness and data comparability.

4.0 SAMPLING PROCEDURES

This section outlines the procedures to be used for the preparation of sampling equipment and containers and for sample preservation. It also provides some of the quality control and operating procedures to be followed for sampling. Detailed field sampling details including the number of samples to be collected, the rationale for sampling, and QC requirements are described in the Field Sampling and Analysis Plan.

4.1 SAMPLE IDENTIFICATION

Each sample collected for this characterization study will be assigned a unique sample tracking number. The identification of the well location and participating gas company will not be identified. All well locations will be blind. GTI will assign each well a project identifier. The project identifier will be a unique single alphanumeric letter that will identify the Devonian Shale well location and company. This unique alphanumeric letter will be provided to the third party environmental consultants to be used in the sample designation.

Flow back Sampling

Fracturing is completed over several days depending on the geological formation. The flow back water is initially removed at a faster rate at the start of production and significantly declines as production continues. It is believed that the volume of water is relative to the concentration. It is assumed that the concentration of the fracturing chemicals remain constant throughout the flow back regardless of the rate of return. However, the increase of in the COI is due to a longer residence time in the applicable formation and not associated to the additives of the fracturing fluids. Therefore, to obtain representative samples of the flow back water samples will be collected on three separate days (i.e., days 1, 5 and 14).

Additionally, a baseline sample of the fracturing fluid will be collected prior to injection. The baseline sample will contain the materials (e.g., water and chemicals) used in the fracturing process. A sample will also be collected from a well in Devonian shale that has been in production for a period of time (i.e., I production fro more than 3 months). The analytical results associated with these samples will assist in the data interpretation.

Quality Assurance

The quality assurance field will only be used to indicate a sample collected for quality assurance purposes.

Quality Assurance/Quality Control Samples will be identified as follows:

EB - Equipment Blank
TB - Trip Blank

The following are sample identification samples.

A05V	Sample collected from company X on day 5 from a vertical well.
CEH	Sample collected from company Y from an existing horizontal well.
TB	Trip Blank.

Each sample container will be marked with a label identifying the specific parameters of interest. The label will record the date of sample collection, alphanumeric identification, parameters to be analyzed, and preservatives, if applicable. Sample bottles should be prelabeled by the laboratory to avoid unnecessary delays.

The specific information for each sample will be documented in the field logbook and on a chain-of-custody form. The sample identification will be correlated in the logbook and chain-of-custody by sample designation, sampling date, time, and location. The analytical parameters for which the sample is to be analyzed and the respective number of sample bottles will be provided on the chain-of-custody sheet.

4.2 SAMPLE CONTAINERS

All new pre-cleaned sample bottles with screw-type Teflon-lined lids will be used for holding and shipping samples. These sample bottles will be supplied by the analytical laboratory, and pre-preserved by the laboratory as necessary.

4.3 FIELD QA/QC SAMPLES

Two types of field QA/QC samples will be collected (i.e., trip blanks and equipment blanks). The following provides a description of the essential field QA/QC samples.

4.3.1 Trip Blanks

Trip blanks are collected only for volatile organic samples. The trip blank is prepared by the laboratory by filling a batch of pre-cleaned 40-ml vials with laboratory-grade water. The vials are transported to the site and returned to the laboratory in the same manner as the environmental sample containers. Any constituents found in the trip blank could be attributed to: a) interaction between the sample and the container, b) contaminated laboratory-grade water, or c) a storage or handling procedure which alters the sample. One trip blank should accompany VOC samples for each sampling event. The trip blank is placed in the cooler that contains samples for volatile organics. At no time after the preparation are trip blanks to be opened before they are returned to the laboratory.

4.3.2 Equipment Blanks

To verify that no constituents are introduced from sampling equipment, equipment blanks are collected by pouring distilled water through the representative sampling device and analyzing for all constituents of interest. One equipment blank will be collected during the characterization study.

4.4 DOCUMENTATION

A number of documents will be used during the characterization study. These documents include: chain-of-custody forms and field data sheets.

Chain-of-custody Forms

The field chain-of-custody form is used to record the custody of all samples collected. This chain-of-custody form documents the transfer of the custody from the sampling personnel to another person, to the laboratory, or another party, such as a courier delivery service.

When the field team sends samples to an analytical laboratory, each shipping cooler containing samples, which are sent under one shipping document, must be accompanied by a chain-of-custody form (Figure 1). These forms document information regarding the origination of samples and those parties having subsequent possession of samples. They also contain information pertaining to these samples, such as project name, name of the individuals collecting the samples, sample identification number, the date and time of collection, the number of sample containers for each parameter of interest for each sample, remarks or observations of samples, if appropriate, the signature of the person relinquishing control of the samples and the person receiving the samples, and the name of the overnight carrier shipping the samples to the laboratory. The original chain-of-custody sheet is sent with the samples. One copy will be submitted to Gas Technology Institute (GTI), and the other copy is stored in the field team files.

5.0 SAMPLE CUSTODY

The primary objective of sample custody is to create an accurate written verified record, which can be used to trace the possession and handling of the samples from the moment of collection through data analysis and reporting.

The field sampler will be personally responsible for the care and custody of the samples collected until they are properly transferred. Samples will be accompanied by a Chain-of-Custody Record.

Upon arrival at the laboratory, samples will be checked in using laboratory custody procedures outlined in the laboratory QAM. The laboratory is required to verify that all samples were received and in good condition. The laboratory should assign a laboratory-specific sample identification. This unique identification guarantees sample anonymity to the analyst of the sample's site.

Once samples have been logged-in and transferred to the proper storage areas, the laboratory department manager is responsible for their proper storage and condition. Copies of the completed Chain-of-Custody Records and an analysis narrative presenting laboratory sample identifications and their correlating field assigned sample identifications should be included in the data package for delivery to the data user.

6.0 ANALYTICAL PROCEDURES

All analyses will be performed using U.S. EPA analytical methods procedures from the following:

> Third Edition (September 1986), as amended by updates 1 (July 1992), II (September 1994), IIA (August 1993), and IIB (January 1995), or the most current SW-846 update;
>
> EPA's "Handbook for Analytical Quality Control in Water and Wastewater Laboratories" (EPA 600/1-79-019);
>
> Standard Methods for the Examination of Water and Wastewater.

Table 1 and Table 2, summarize the list the constituents of interest (COIs) associated with the characterization study for the flow back water from the wells of the Devonian shale and the required reporting limits to be reported by the laboratory. Method selection was based on the following factors: reliability in identification and quantifications, and comparability of sample results and best achievability of the lower of federal Maximum Contaminant Levels (MCLs).

All procedures for environmental sample handling, storage, and documentation while in the laboratory's custody and deliverable requirements upon delivery of the data to the user are stated in the laboratory QAMs.

7.0 CALIBRATION PROCEDURES AND FREQUENCY

All field and laboratory equipment are calibrated before use to ensure proper operating conditions. Laboratory instrument calibration procedures are presented in the laboratory QAMs. Field calibration procedures and frequencies should be followed in accordance with the manufactures specifications. Field calibrations must be completed each day at a minimum. pH meters are required to be calibrated or verified every two hours at a minimum.

7.1 PREPARATION OF STANDARDS

All analytical methods must be validated at some point by the use of calibration standards. A calibration standard is made by the appropriate dilution of a pure substance, the purity of which is traceable to an NBS or U.S. EPA standard. Because of the high sensitivity of many analytical instruments, the calibration standard is an extremely dilute version of the pure compound. Because of the high dilution required to be within the linear range of the instrument, the preparation of the calibration standard is frequently made by serial dilution rather than in a single step. In order to provide standard solutions at sufficiently low concentrations, a minuscule amount of the pure substance will be required, the measurement of which is subject to extreme error. Thus, it is preferable to deal with potential dilution errors, rather than with the large error associated with the measurement of a very small amount of the pure substance.

The initial standard is usually obtained either as a pure material or as a prepared certified solution of a given concentration of the pure compound or compounds. In preparing the stock solution of the calibration standard, great care must be exercised in measuring weights and volumes as accurately as possible, since all of the analyses following the calibration will be based on the accuracy of the calibration, and the accuracy of the analytical data is dependent on the calibration curve. It is the analyst's responsibility to assure that all standards used are within the standard solution holding time, and to prepare fresh standard solutions whenever necessary. In preparing working solutions, or using working solutions, the analyst must check for signs of deterioration of the standard, such as cloudiness, precipitation, or discoloration. The standard must also be periodically compared with previous runs of standards, and with independently prepared standards to assure that response factors fall within a historically accepted range.

7.2 CORRECTIVE ACTION

There are many laboratory functions that may require corrective action. The decision to undertake corrective action, and the ensuing action must be documented so that traceability can be maintained. The point of originating the corrective action varies, depending upon the mode of detection that such action is necessary. It is generally the role of either the Laboratory QA Officer or the Laboratory Department Manager to initiate such action. Those actions that affect the quality of the data will be recorded and the record maintained by the Laboratory QA Officer.

The general procedures for appropriate laboratory corrective actions and identification of potential problems are presented in the analytical laboratory QAM.

8.0 DATA EVALUATION/VALIDATION

Data are typically validated by the laboratory and field personnel. First, during the field operations, field measures will be validated at the time of collection by the field sampler by verifying the use of standard operating procedures for the sampling effort and using field QC checks. Second, laboratory analytical results will be validated by the Laboratory Department Manager or the analyst who is the specific analytical task leader.

8.1 FIELD DATA VALIDATION

Validation of field obtained data, as well as ongoing QA/QC checks of environmental samples being taken, is performed on field data. All field data are reviewed during the time of collection and second, all data are reviewed by secondary field personnel if multiple personnel are present. Corrections in the field logbooks will be removed by placing a single line through the entry, initialing and dating the correction. If information is added without a correction being necessary that entry will be initialed and dated to indicate that it was not entered at the original time of data entry. Entries should never be “whited out” or made in pencil.

8.2 LABORATORY DATA VALIDATION

The individual Laboratory Department Managers should validate all laboratory data, prior to reporting. Some of the following QA/QC measures are reviewed or procedures are typically used:

- A standard curve is prepared prior to sample analysis;
- The standard regression coefficient is within the acceptable range;
- Standard reference materials are analyzed at the proper frequencies and acceptable results are obtained;
- The reagent blanks are analyzed at the proper frequency;
- Precision requirements of this plan are met;
- Accuracy requirements of this plan are met;
- Completeness requirements of this plan are met;
- Samples are analyzed within the proper sample holding times;
- All calculations are verified as correct;
- Proper units are reported; and
- The proper methodologies were used.

Besides this review of analytical results and project specific precision, accuracy, and completeness requirements, the Laboratory Department Manager should perform unannounced audits of report forms and other data sheets as well as regular reviews of instrument logs, performance test results, and analysts’ performance. Any review of analytical results or internal QA/QC checks that indicate problems, immediate corrective actions should be taken and all data collected since the previous approved QC audits should be reviewed for validity. Specific laboratory procedures for validation of the analytical data generated are described in the laboratory QAMs.

8.3 INDEPENDENT DATA VALIDATION

The laboratory will provide DQO Level 3 (i.e., CLP Like) data packages. However, the data packages will not be validated at this time. Data validation procedures following the applicable guidance from the current U. S. EPA's *Contract Laboratory Program, National Functional Guidelines for Organic Data Review* and the U. S. EPA's *Contract Laboratory Program, National Functional Guidelines for Inorganic Data Review* will be performed, if required.

8.4 DATA REPORTING

Analytical Laboratory

Once the data have been validated internally by the laboratory, all of the results are electronically or automatically entered into the laboratory's data management system where they are stored prior to reporting. When all analyses are completed for data storage, the Laboratory Director (or his/her designee) will issue a final data report including a descriptive case narrative. He or she will then issue the report to the data user. All applicable QC data should be included with the final report.

The data reports generated for this project should contain all pertinent information for the data user to determine the applicability and usability of the data for its intended purposes. For this reason, a specified and uniform data reporting format should be implemented. For this project, DQO levels III data packages will be reported as a Level IV (CLP-like) deliverable to facilitate data validation, if needed. The following criteria and information should be supplied, at a minimum, for data reports generated for this project:

1. A descriptive case narrative identifying any problems encountered during internal data validation (as described above);

2. Completed and legible chain-of-custodies for all analyses contained within each submitted data package;

3. A lab sample chronicle indicating which analyses were requested and performed for the samples contained in the data package;

4. A summary of the laboratory sample identifications and the correlating field sample identifications;

5. A summary of all applicable analytical results reported in the correct number of significant figures, reporting units; and

6. Included in the individual sample reporting results should be the complete sample identifications, the sample dilutions (if necessary), and the individual sample analysis dates.

8.4.1 LEVEL I REPORTING

Summary reporting only will be provided. Bulleted items above are required under this DQL.

8.4.2 LEVEL II REPORTING

Summary reporting only will be provided. The data package reporting requirements are the same as Level I except legible and calculated QA/QC summaries for laboratory blanks, surrogate recoveries (if applicable), laboratory control sample recoveries, and matrix spike/matrix spike duplicate recoveries (or matrix spike recovery and laboratory duplicate results) must also be supplied under this DQL.

8.4.3 LEVEL III REPORTING

The following summary forms and raw data deliverable requirements will apply for Data Quality Level III.

The following forms are required for all analyses using Gas Chromatography/Mass Spectroscopy methods.

- Narrative and sample identification cross reference;
- Copies of Chain-of-Custody documentation;
- Laboratory chronicle;
- Method summaries and references;
- Organic analysis data sheet for samples and blanks (with TICs as required);
- System monitoring compound/surrogate recoveries summary;
- Matrix spike/Matrix spike duplicate summary or any lab duplicate;
- QC Check Sample summary;
- Method blank summary and results;
- Instrument performance check summary;
- Initial calibration summary for all constituents of interest;
- Continuing calibration check summary for all constituents of interest;
- Internal standard area and RT summary;
- Extraction/preparation logs;
- The handwritten calculation for at least one positive result in one sample at a rate of one calculation per twenty samples or per data package (whichever is greater) per fraction (e.g., VOC or SVOC); and
- Raw data including run logs, mass spectra, quantitation reports and chromatograms for

samples, as well as any raw data used to complete the hand written calculation.

The following forms are required for all total metal analyses.

- Narrative and sample identification cross reference;
- Copies of Chain-of-Custody documentation;
- Laboratory chronicle;
- Method summaries and references;
- Inorganic analysis data sheets;
- Initial and continuing calibration verification;
- Initial and continuing calibration blanks and preparation blank summary;
- ICP interference check sample summary;
- Spike sample recovery;
- Duplicate results summary;
- Laboratory Control Sample summary;
- Standard addition results summary, when applicable;
- ICP serial dilutions;
- Instrument detection limits;
- ICP inter-element correction factors summary;
- Preparation log;
- Analysis run log;
- The hand-written calculation for at least one positive result in one sample at a rate of one calculation per twenty samples or per data package (whichever is greater) per method (e.g., GFAA/ICP/CU); and
- Raw data.

The following data and summary forms will be submitted by the laboratory for inorganic non-metals analyses or other analyses not discussed above:

- Narrative and sample identification cross reference;
- Copies of Chain-of-Custody documentation;
- Laboratory chronicle;
- Method summaries and references;
- Analysis data sheets;
- Calibration summaries; and
- Calibration equation and curve plot;
- Blank results summary;
- Sample spike recovery, where applicable;
- Duplicate sample results, where applicable; and
- Laboratory control sample summary where applicable.

9.0 QUALITY CONTROL PROCEDURES

Quality control (QC) procedures and checks are used to verify the accuracy of investigation data. Field QC checks are used to identify potential problems with sampling procedures such as the inconsistent use of sampling standard operating procedures or field introduced sample or water supply contamination and/or problems with sample homogeneity or representativeness. Laboratory QC checks are used to identify potential problems with analytical procedures such as the misapplication of required analytical methodologies or other laboratory related problems which could result in inaccurate or imprecise data reported. The laboratory QC checks and procedures presented in this section are required for most of the applicable methods, but the frequency of the QC checks should follow procedures outlined in the laboratory QAMs.

9.1 FIELD QC CHECKS

To check the quality of data from field sampling efforts, field blanks and field duplicate samples will be collected for analysis. These samples will be treated as separate samples for identification, logging, and shipping. Analytical results on blanks and duplicates will be reported with the appropriate field sample data. The number of these samples, when required, and their use was described in Section 5.0.

9.1.1 EQUIPMENT BLANKS

The equipment blank provides a check on possible sources of sample contamination. The equipment blanks should be collected in the worst-case scenario. The reason for performing equipment blanks in the most impacted area is to attempt to simulate a worst-case scenario regarding contributions from site condition or from improperly cleaned sampling equipment to sample contamination. One equipment blank will be for this project. Equipment blanks should be handled, transported, and analyzed in the same manner as the samples with which they are associated.

The equipment blank water must be maintained at 4 (±2)°C following collection and during shipment. Holding times for individual parameters are dictated by the specific analytical method being used. The holding-time clock begins at the time of sample collection of the equipment blank.

9.1.2 TRIP BLANKS

Trip blanks are used to check for sample contamination introduced by the sample containers, by the sampling equipment, or by the sampling environment. Trip blanks travel to the site with the empty sample bottles and return from the site with the collected samples in an effort to simulate sample handling conditions. Trip blanks are collected in association with samples that are to be analyzed for volatile organic compounds. Potential sources of sample contamination are from the laboratory-grade reagent water, sample containers, field or laboratory ambient air, laboratory reagents, or cross contamination during shipping, handling, preparation or analysis. A trip blank should accompany VOC samples for each sampling event.

The trip blank water must be maintained at 4 (±2)°C through sample collection activities and during shipment. Holding times for individual parameters are dictated by the specific analytical method being used. The holding-time clock begins at the time of sample collection of the oldest sample in the sampling container.

9.2 INTERNAL LABORATORY QC CHECKS

The QC check frequencies and requirements specified in the following sections is a general description only. The laboratory will follow the internal QC checks specified in its QAM for each analysis type employed. However, these QC checks must meet, at a minimum, the requirements specified in the respective U.S. EPA analytical methods.

The following internal laboratory QC checks are performed for most analyses, whenever applicable, to ensure the measurement systems are under control:

- Initial and continuing calibrations;
- Preparation/method blanks;
- Matrix spike and matrix spike duplicate or matrix spike and laboratory duplicate analysis, as appropriate;
- Surrogate spike standard performance evaluation (for organic analyses only); and
- Calibration check compounds and reagent blanks (for organic analyses only).

Additional internal laboratory QC checks are typically performed for most analyses, as required by the associated analytical method. Only the most common QC checks are generally described below.

9.2.1 INITIAL AND CONTINUING CALIBRATION

Each measurement system must be calibrated immediately prior to use and be shown to maintain the calibration throughout the course of the analysis. For the organic parameter methods, all target compounds will be checked during initial and continuing calibrations. Calibration procedures and frequencies is discussed for the various analysis types in the laboratory QAMs. An initial calibration will be performed prior to WSC sample analyses. Continuing calibrations will be typically analyzed at a minimum frequency of one every ten samples. For CLP GC/MS analysis, calibration checks are only required once every 12 hours of analysis.

9.2.2 Preparation/Method Blanks

A preparation or method blank is run with each batch of samples received for analysis. Compound or analyte responses observed in the blank at levels above the reportable detection limit are reviewed for possible laboratory contamination. If high blank values are observed, laboratory glassware and reagents may need to be checked for contamination and the analysis of future samples halted until the system can be brought under control. A high blank value is typically defined as a value greater than the method detection limit. A preparation and/or method blank will be prepared at a frequency of one per 20 samples or one per day, whichever is greater.

9.2.3 Matrix Spike And Duplicate (Or Matrix Spike Duplicate) Analysis

For all analyses where matrix spiking is possible, 1 in 20 samples is analyzed as matrix spikes and matrix spike duplicates or 1 in 20 samples is analyzed as matrix spikes and duplicates. Field personnel must provide additional volume for the laboratory to complete a MS/MSD. The percent recovery for spiked samples is calculated using the equations given in Section 12.0 and compared to the accuracy criteria specified in the QAM for the associated analytical method. The relative percent difference of replicate spikes or replicate analytical results are calculated using the equations given in Section 12.0 and compared to the precision criteria specified in the laboratory QAMs (Appendix QAPP-1 and following) for the associated analytical method.

9.2.4 Surrogate Spike Standard Performance Evaluation

Surrogate standards are defined as nonpriority pollutant compounds used to monitor the percent recovery efficiencies of the analytical procedures on a sample-by-sample basis. Surrogate standard determinations are performed on all samples and blanks for organic analyses. All samples are fortified with surrogate spiking compounds before purging or extraction to monitor the preparation and analysis of samples.

Surrogate compounds and recovery levels for the associated analyses are presented in the laboratory QAM (surrogate recovery limits are method- and media-specific and are either specified in the method or are calculated annually by the analytical laboratory as described in the analytical method). When the surrogate recovery level is outside of the control limits on the initial analysis, the laboratory must take the following actions for all organic analyses for samples:

- Check calculations to assure there are no errors, check internal standard and surrogate spiking solutions for degradation or contamination and check instrument performance; and

- Recalculate or reinject/repurge the sample or re-extract and reanalyze the sample.

9.2.5 Calibration Check Compounds And Reagent Blanks

These calibration check compounds and reagent blanks are analyzed periodically throughout the course of the analysis, depending on the required analysis. The exact frequencies and methods of use are presented in the laboratory QAM.

10.0 PERFORMANCE AND SYSTEM AUDITS

Two types of audit procedures may be conducted during any environmental investigation: performance audits and system audits. These audits may be performed on the laboratory as well as field activities. A description of the laboratory's specific guidance for Performance and System Audits will be presented in laboratory QAMs. General procedures for laboratory performance and system audits are presented below.

10.1 PERFORMANCE AUDITS

10.1.1 Laboratory Performance Audits

Laboratory performance audits are typically conducted by the Laboratory QA Officer on a regular basis. Each laboratory analyst is given a performance evaluation sample containing analytes for the parameters which he/she usually performs. These audit samples are used to identify problems in sample preparation or analysis techniques or methodologies which could lead to future analytical problems.

Additionally, the laboratory performance audits include verification of each analyst's record keeping, proper use and understanding of procedures, and performance documentation. Corrective action will be taken for any deficiencies noted during the audit.

10.2 SYSTEM AUDITS

10.2.1 Laboratory System Audits

Laboratory system audits are typically conducted by the Laboratory QA Officer. These audits are used to ensure that all aspects of the Laboratory's QAM are operative. This involves a thorough review of all laboratory methods performed and documentation to confirm that work is performed according to project specifications.

In some cases, outside certification agencies conduct performance and system audits to verify contract compliance or the laboratories' ability to meet certification requirements on methods of analysis and documentation. Results of these outside certification audits may be reviewed at any time as a check on the laboratory’s internal auditing procedures.

11.0 ASSESSMENT PROCEDURES FOR DATA ACCEPTABILITY

The following discussion describes the procedures that will be employed to evaluate the precision, accuracy, and completeness of the generated data.

11.1 PRECISION

Precision is a measure of agreement among individual measurements of the same property under prescribed similar conditions. Precision is assessed by calculating the relative percent difference (RPD) of replicate spike samples or replicate sample analyses according to, the following equation:

$$RPD = \frac{R1 - R2}{(R1 + R2)/2} \times 100$$

where

R1 = result 1

R2 = result 2

11.2 ACCURACY

Accuracy is a measure of the closeness of an individual measurement to the true value. Accuracy is measured by calculating the percent recovery (%R) of known levels of spike compounds as follows:

$$\%R = \frac{\text{concentration of spike sample - concentration of unspiked sample}}{\text{concentration of spike added}} \times 100$$

11.3 COMPLETENESS

Completeness is a measure of the amount of valid data obtained from a measurement system, expressed as a percentage of the number of valid measurements that should have been collected. As is specified in Section 4.2, more than one completeness check can be evaluated. It is calculated as follows:

$$\text{Completeness (\%)} = \frac{\text{number of valid samples reported}}{\text{total number of samples analyzed}} \times 100$$

11.4 QUALITY CONTROL CHARTS

Quality control charts can be prepared after every 20 analytical determinations to graphically evaluate precision and accuracy criteria. The charts are prepared by calculating the mean value of the determinations and setting control limits at ± 3 standard deviations from that mean. The following equations are used:

$$mean = \bar{x} = \sum_{i=1}^{n} \chi_i/\eta$$

$$standard \quad deviation = \sqrt{\frac{1}{n-1} \sum_{i=1}^{n} (x_i - \bar{x})^2}$$

The control limits should be within acceptance limits or ranges presented in the as yet unselected laboratory's QAM. If the values are found to be outside these limits or ranges, the measurement system is examined to determine if possible problems exist.

12.0 PREVENTIVE MAINTENANCE

Periodic preventive maintenance is required for equipment whose performance can affect results. Instrument manuals are kept on file for reference if equipment needs repair. Troubleshooting sections of manuals are often useful in assisting personnel in performing maintenance tasks.

12.1 FIELD

Field sampling personnel will be responsible for preventive maintenance of all field instruments. The field sampling personnel will protect the instruments by placing them in portable boxes and/or protective cases.

All field equipment will be subject to a routine maintenance program, prior to and after each use. The routine maintenance program for each piece of equipment will be in accordance with the manufacturer's operations and maintenance manual. All equipment will be cleaned and checked for integrity before and after each use. Necessary repairs will be performed immediately after any defects are observed, and before the item of equipment is used again.

Equipment parts with a limited life (such as batteries, membranes and some electronic components) will be periodically checked and replaced or recharged as necessary according to the manufacturer's specifications.

Preventive maintenance is important since it provides for a longer useful life of the equipment and helps to ensure a successful field sampling and testing program. Each piece of field equipment will have its own log sheet which contains the equipment identification and the type of maintenance performed. Since most equipment is used on an irregular basis, all equipment will be properly stored when not in use.

12.2 LABORATORY

All major laboratory instruments should normally be under service contract so that trained professionals are available on call to minimize instrument downtime. Other preventive maintenance schedules and/or procedures for laboratory equipment is presented in the laboratory QAMs (Appendix QAPP-1 and following).

13.0 CORRECTIVE ACTION

Corrective action procedures are divided into two subgroups: methods corrective action and systems corrective action. These corrective actions are implemented whenever system or performance audits note deficiencies or when QC procedures indicate a potential analytical problem. The laboratory guidance on Corrective Action procedures is presented in the laboratory QAMs.

14.0 QA REPORTS TO MANAGEMENT

This QAPP provides a documentable mechanism for the assurance of quality work performed at for the characterization study. Audit reports will be provided by the Laboratory Director (or his/her designee) as a means of tracking program performance, as applicable, or if needed. Additionally, periodic assessments of measurement data accuracy, precision, and completeness and significant QA/QC problems will be performed and reported to laboratory and/or project management, if needed.

Field QA reports will not be necessary considering the expected size and length of any individual sample collection activities. Any problems noted during sampling will be immediately communicated to GTI, so GTI can take whatever corrective actions necessary.

Upon completion of the project-specific Work Plans, a final QA/QC report will be issued, assessing the overall degree of project conformance to specifications and the impact of any non-conformances that may affect management decisions.

The final storage location of the files will be maintained at GTI’s office in Chicago. The files will be maintained for a period of at least three years.